# Optimization and calibration of high-temperature liquid chromatographic separation of polypropylene and propylene based copolymers

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*"The development of polymers is perhaps, the biggest thing chemistry has done, where it has had the biggest effect on everyday life"*

Lord Todd
President of the royal society of London

*Dedicated to all my colleagues, gurus, friends and family.*

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## Table of Contents

| | |
|---|---|
| CC | Chemical Composition |
| CCD | Chemical Composition Distribution |
| MMD | Molar Mass Distribution |
| PGC | Porous graphitic carbon |
| BN | Boron nitride |
| $MoS_2$ | Molybdenum disulphide |
| PE | Polyethylene |
| PP | Polypropylene |
| *it*-PP | Isotactic Polypropylene |
| *st*-PP | Syndiotactic Polypropylene |
| *at*-PP | Atactic Polypropylene |
| PP-HI | High Impact Polypropylene |
| PVC | Polyvinyl Chloride |
| EP | Ethylene-Propylene copoymer |
| EPDM | Ethylene-Propylene-Diene |
| EO | Ethylene-Octene copolymer |
| PS-DVB | Poly (styrene-divinylbenzene) |
| HPLC | High Performance Liquid Chromatography |
| LAC | Liquid Adsorption Chromatography |
| HT-HPLC | High Temperature High Performance Liquid Chromatography |
| HT-LAC | High Temperature Liquid Adsorption Chromatography |
| SEC | Size Exclusion Chromatography |
| HT-SEC | High Temperature Size Exclusion Chromatography |
| TREF | Temperature Rising Elution Fractionation |
| CRYSTAF | Crystallization Analysis Fractionation |
| CEF | Crystallization elution fractionation |
| HT 2D-LC | High-Temperature Two-Dimensional Liquid Chromatography |
| HT-AF4 | High Temperature Asymmetrical Flow Field-Flow Fractionation |
| TGIC | Temperature gradient interaction chromatography |
| DSC | Differential Scanning Calorimetry |
| TCB | 1,2,4-trichlorobenzene |
| ODCB | o-dichlorobenzene |

| | |
|---|---|
| 2E1H | 2-ethyl-1-hexanol |
| RI | Refractive Index Detector |
| IR | Infrared Detector |
| ELSD | Evaporative Light Scattering Detector |
| Visc | Viscometer Detector |
| LS | Light-scattering |
| FTIR | Fourier Transform Infrared Spectroscopy |
| LCB | Long Chain Branching |
| SCB | Short Chain Branching |
| HDPE | High Density Polyethylene |
| LDPE | Low Density Polyethylene |
| LLDPE | Linear Low Density Polyethylene |
| EVA | Ethylene Vinyl Acetate |
| EMMA | Ethylene Methyl Methacrylate |
| M | Molar mass |
| $M_n$ | Number average molar mass |
| $M_w$ | Weight average molar mass |
| $M_p$ | Molar mass at peak maximum |
| Đ | Dispersity Index |
| $V_{mob}$ | Volume of the mobile phase |
| $V_{stat}$ | Volume of the stationary phase |
| $V_R$ | Retention volume |
| K | Distribution (partition) equilibrium coefficient |
| $\Delta G_0$ | Standard Gibbs free energy change |
| $\Delta H^0$ | Standard enthalpy change |
| $\Delta S^0$ | Standard entropy change |
| $V_{stat,\ interactive}$ | Volume of the “interactive part” of the total stationary phase |
| $V_{TL}$ | Transfer loop volume |
| $F_{LAC}$ | Solvent flow rate in HT-LAC column |
| $\Delta t$ | Interval between two SEC injections |
| $N_{LAC}$ | Number of HT-LAC fractions |
| $V_{grad}$ | Volume of the gradient |

| | |
|---|---|
| $t_{HT\ 2D\text{-}LC}$ | Time required for one HT-LAC analysis |
| S | Standard deviation |
| $Y_i$ | Value of $i^{th}$ data in full data set (i = [1,2, ….,N]) |
| $\mu$ | Average of the data set |
| N | Total number of points in the data set |
| $E_{i,j}$ | Element of the matrix |
| $H_{i,j}$ | IR response in an element $E_{i,j}$ of the matrix |
| $m_{i,j}$ | Mass of the polymer in an element $E_{i,j}$ |
| $M_{i,j}$ | Molar mass of the polymer in an element $E_{i,j}$ |
| LOQ | Limit of quantification |
| $V_{SEC}$ | Elution volume in SEC |
| $E_{PMAX}$ | Elution volume at peak maximum |
| $m_1$ | Mass of polymer calculated from the matrix corresponding to $EP_{39.8}$ |
| $m_2$ | Mass of polymer calculated from the matrix corresponding to $EP_{59.7}$ |
| $m_T$ | Total mass of polymers calculated from the matrix corresponding to $EP_{39.8}$ and $EP_{59.7}$ |
| $m_D$ | Difference in mass of polymers calculated from the matrix corresponding to $EP_{39.8}$ and $EP_{59.7}$ |
| $m_I$ | Identical mass of polymers calculated from the matrix corresponding to $EP_{39.8}$ and $EP_{59.7}$ |
| $D_1$ | Mass of unique segments calculated from the matrix corresponding to $EP_{39.8}$ |
| $D_2$ | Mass of unique segments calculated from the matrix corresponding to $EP_{59.7}$ |
| EC | Ethylene content |
| $EC_n$ | Number average ethylene content |
| $EC_w$ | Weight average ethylene content |

## 1 Zusammenfassung

Polyolefine sind, gemessen am Produktionsvolumen, die weltweit bedeutendste Gruppe von Polymeren. Sie stellen mehr als 50 % des globalen Polymermarktes, wobei Polypropylen (PP) und Propylen-basierte Copolymere zwei der wichtigsten Vertreter der Polyolefinfamilie sind. Moderne Katalysator- und Reaktortechnologien haben es ermöglicht die molekularen Heterogenitäten (d.h. Verteilung der chemischen Zusammensetzung (Chemical Composition Distribution (CCD)) und Molmassenverteilung (Molar Mass Distribution (MMD)) in Polyolefinen zu kontrollieren. Geringe Unterschiede dieser molekularen Parameter können zu deutlichen Verbesserungen der Anwendungseigenschaften dieser Materialien führen.

Stand der Technik ist es die MMD von Polymeren unter Verwendung von Größenausschlusschromatographie (Size Exclusion Chromatography (SEC)) zu bestimmen. SEC trennt die Makromoleküle nach ihrem hydrodynamischen Volumen im Lösungsmittel, was wiederum ein indirektes Maß für deren Molmassen ist. Da Polyolefine im Allgemeinen aufgrund ihrer teilkristallinen Natur bei Raumtemperatur unlöslich sind, erfordert die Untersuchung mittels SEC erhöhte Temperaturen (Hochtemperatur-SEC, HT-SEC).

Copolymere werden aus mehr als einem Monomer hergestellt, weshalb die CCD ein überaus wichtiger, molekularer Parameter bei der Ermittlung von Struktur-Eigenschafts-Beziehungen ist. Es ist Stand der Technik, auf Kristallisation basierende Methoden, d.h. analytische Kristallisationsfraktionierung (Crystallization Analysis Fractionation (CRYSTAF)), Kristallisations-Elutions-Fraktionierung (Crystallization Elution Fractionation (CEF)) und Temperature Rising Elution Fractionation (TREF),

zu verwenden, um die CCD von teilkristallinen Polyolefinen zu bestimmen. Bei diesen Methoden beruht die Auftrennung darauf, dass die Kristallisierbarkeit (Kristallisationstemperatur) der Makromoleküle aus der Lösung von deren Comonomergehalt abhängt. Aufgrund dieses Trennprinzips können auf Kristallisation basierende Methoden können jedoch nicht verwendet werden, um amorphe Copolymere zu trennen. Zudem unterliegen sie Einschränkungen durch den Einfluss von Co-Kristallisationseffekten.

Seit einigen Jahren wird die Eignung der Hochtemperatur-Flüssigkeitsadsorptionschromatographie (High Temperature Liquid Adsorption Chromatography (HT-LAC)) zur Trennung von weniger kristallinen oder sogar amorphen Olefin-basierten Copolymeren (z.B. Ethylen-Propylen-(EP)-Copolymere) intensiv erforscht. Als stationäre Phase wird dabei häufig poröser graphitischer Kohlenstoff (Porous Graphitic Carbon (PGC)), der kommerziell als Hypercarb™ verfügbar ist, verwendet.

Flüssigkeitschromatographie bei kritischen Bedingungen (Liquid Chromatography at Critical Conditions (LCCC)) ist eine intermediäre Trennungsweise, die zwischen SEC (Entropie-getriebener Prozess) und LAC (Enthalpie-getriebener Prozess) angesiedelt ist. Unter diesen Bedingungen kompensieren sich die entropischen und enthalpischen Effekte. In dieser Arbeit wurden potentiell geeignete mobile Phasen für die LCCC von Isotaktischem (*it*-PP) und Syndiotaktischem Polypropylen (*st*-PP) identifiziert. Drei verschiedene Methoden (gemäß Bashir, Cools und der SEC-LAC-Graph-Ansatz) wurden verwendet, um kritische Bedingungen für Polypropylen bei 160 °C zu bestimmen. 2-Octanol und 2-Ethyl-1-Hexanol (2E1H) wurden dabei als adsorptionsfördernde Lösungsmittel eingesetzt und 1,2-Dichlorbenzol (ODCB) sowie

1,2,4-Trichlorbenzol (TCB) als desorptionsfördernde Lösungsmittel. Anhand der erhaltenen Daten konnte ermittelt werden, dass ein geringerer TCB-Anteil im Lösungsmittel nötig ist, um kritische Bedingungen für *it*-PP zu erreichen, als dies bei Verwendung von ODCB der Fall ist. In gleicher Weise wurde festgestellt, dass 2-Octanol ein geringfügig schwächerer Eluent als 2E1H ist. Auch der Einfluss der Temperatur auf die kritischen Bedingungen für *it*-PP wurde untersucht und es wurde eine lineare Abhängigkeit zwischen dem Anteil an desorptionsfördendem Lösungsmittel und der Temperatur gefunden.

Basierend auf diesen Ergebnissen wurde eine neue Methode zur Bestimmung der Bedingungen für LCCC vorgeschlagen, die lediglich eine einzige Polymerprobe hoher Masse benötigt, und es erstmals ermöglicht den LCCC-Trennmodus in einer isokratischen Herangehensweise zu identifizieren. Damit ist man unabhängig von Serien wohl definierter Proben, die Elugramme mit klar definierter Form zeigen, oder bei denen die Elutionsvolumina sehr exakt ermittelt werden können. Diese neue Methode wurde verwendet um Bedingungen für die LCCC von *it*-PP und *st*-PP in 2-Octanol/ODCB und 2E1H/ODCB, sowie von Polyethylen (PE) in n-Decan/TCB zu bestimmen.

Die Verwendung eines Lösungsmittelgradienten bei der HT-LAC macht es schwierig einen quantitativen Detektor (z.B. Infrarot-(IR)) zu verwenden, um das aus der chromatographischen Säule austretende Lösungsmittel kontinuierlich zu untersuchen, da die meisten adsorptionsfördernden mobilen Phasen nicht IR-transparent sind. Eine Kopplung der HT-LAC mit der HT-SEC (HT-LAC x HT-SEC), auch bekannt als 2-dimensionale Chromatographie bei hoher Temperatur (High Temperature Two Dimensional Liquid Chromatography (HT 2D-LC)), wurde verwendet, um die

bivariate CCD x MMD von Polyolefinen zu untersuchen. Die HT 2D-LC bietet grundsätzlich die Möglichkeit nach der zweiten Dimension der Trennung einen IR-Detektor zu verwenden (HT 2D-LC-IR), da die Lösungsmittelzusammensetzung in der HT-GPC quasi-isokratisch ist.

In dieser Arbeit wurde im Rahmen eines Modellansatzes eine PP-Probe mit hoher Schlagzähigkeit (high impact PP (PP-Hi, d.h. *it*-PP/ EP entsprechend 50/ 50 Gew.-%) in ihre Bestandteile getrennt. Dabei wurde in der ersten Dimension der HT 2D-LC-IR der LCCC für *it*-PP eingesetzt. Das teilkristalline *it*-PP eluierte im LCCC-Modus, während der EP-Anteil auf der stationären Phase adsorbiert wurde und erst in reinem desorptionsfördendem Lösungsmittel (ODCB) eluierte. Dieser Ansatz kommt ohne einen linearen Lösungsmittelgradienten aus, sodass eine Trennung unter Verwendung einer isokratischen Pumpe möglich war.

EP-Copolymere, die mit verschiedenen Katalysatoren hergestellt wurden, können einzigartige (d.h. von verschiedener Molmasse und chemischer Zusammensetzung) und identische (d.h. von gleicher Molmasse und chemischer Zusammensetzung) Segmente in unterschiedlichen Anteilen enthalten. Bis jetzt existierte keine Methode, die es erlaubte diese einzigartigen und identischen Segmente zu quantifizieren. Eine neue Methode (Matrix-Ansatz, siehe nächster Absatz) für die Quantifizierung der identischen und einzigartigen Segmente in EP-Copolymeren unter Verwendung von HT 2D-LC-IR wurde vorgeschlagen. Dazu wurden im ersten Schritt die Parameter der HT 2D-LC-IR mit dem Ziel, die Überlappung des Lösungsmittelpeaks mit dem eluierenden Polymer zu elimieren, optimiert. Eine HT-LAC-Flussrate von 0,05 mL/min und eine HT-SEC-Flussrate von 2,5 mL/min wurden als Optimum für die Trennung von EP-Copolymeren nach deren CCD x MMD gewählt. Kalibrationen der

Elutionszeiten in der HT-SEC- und der LAC-Dimension sowie des Ansprechverhaltens des Detektors wurden durchgeführt. Dazu wurde eine neue Methode zur Kalibrierung des Ansprechverhaltens des IR-Detektors in Abhängkeit von der injizierten Masse an Polymer entwickelt. Ein entscheidender Vorteil dieser neuen Methode ist, dass nur eine einzige Injektion notwendig ist, was die Zahl möglicher Fehlerquellen vermindert und einen geringeren Wert für die Bestimmungsgrenze (0.03 mg/ mL) liefert.

Im Allgemeinen werden die Daten aus einer HT 2D-LC-IR-Analyse von Polymeren als Konturplots dargestellt. Wandelt man diese in Matrizen um, wird es möglich mathematische Operationen (z.B. Additionen und Subtraktionen) durchzuführen, mit dem Ziel Unterschiede hinsichtlich der molekularen Heterogenitäten in quantitativer Weise zu untersuchen. Der Matrix-Ansatz wurde nicht nur verwendet, um Informationen über die Gesamtheit der Fraktionen an identischen und einzigartigen Segmenten in EP-Copolymeren zu erhalten, sondern auch dazu Durchschnittswerte hinsichtlich Molmasse und chemischer Zusammensetzung dieser Segmente zu bestimmen. Solche quantitativen Daten sind eine Voraussetzung dafür Struktur-Eigenschafts-Beziehungen von Copolymeren ermitteln zu können.

Die Suche nach alternativen stationären Phasen, die im Vergleich zu Hypercarb™ verbesserte Selektivitäten zeigen könnten, ist von höchstem Interesse für Wissenschaftler, die auf dem Gebiet der HT-LAC arbeiten. Eine Arbeitshypothese ist, dass stationäre Phasen, die ähnlich wie Hypercarb™ eine auf atomarer Ebene flache Oberfläche (Atomic Level Flat Surface (ALFS)) zeigen (Bornitrid (BN) und Molybdändisulfid ($MoS_2$)), die am besten geeigneten Kandidaten für die Adsorption von Polyolefinen sind. In dieser Arbeit wurden diese stationären Phasen unter Verwendung verschiedener mobiler Phasen im Hinblick auf ihre Eignung für HT-LAC-

Untersuchungen von Polyolefinen getestet. Die mit diesen stationären Phasen gefundene Elutionsreihenfolge (*it*-PP < *at*-PP < *st*-PP < PE) war die gleiche wie bei Hypercarb™ unter Verwendung der untersuchten mobilen Phasen. Insgesamt war die ermittelte Adsorption auf den stationären Phasen jedoch im Vergleich zu Hypercarb™ schwächer.

## 2 Introduction

Polypropylene (PP) has become one of the largest and fastest growing thermoplastics in the market place today as it offers a good price/performance ratio and in many respects better performance properties (e.g., high melting point) over other polyolefins (e.g., Polyethylene (PE)).[1] Highly Isotactic PP (*it*-PP) is brittle at low temperatures and has low impact strength. Improving the latter by incorporating discrete rubbery domains in the PP matrix opened the door to apply PP materials in applications where mechanical performance is a crucial criterion. Being light weight and corrosion resistant (in aqueous environments) High Impact PP (PP-HI) has replaced metal in a number of car components in the last decades. Weight reduction paired with high passenger safety is an important trend in the automotive sector, and polymers are able to fulfill this need at reasonable costs, with PP-HI being at the frontline of development.[1-3]

New types of propylene based copolymers may be used in previously impossible applications, for example, advanced PP grades may substitute plasticized Polyvinyl Chloride (PVC) and may replace glass-fiber reinforced polyamide for air-intake manifolds in cars.[2] PP random (PP-R) copolymers, which contain very low amounts of a second monomer (e.g., ethylene or 1-butene from 0.5 to 5 wt. %), provide a broad range of characteristics and are used in a wide range of applications (e.g., packaging). Ethylene-Propylene (EP) copolymers, a term which in the commercial sense is generally used for EP rubbers, are more flexible compared to PP homopolymer. Ethylene-Propylene-Diene-Monomer (EPDM) rubbers, which are terpolymers of propylene, show excellent resistance towards ozone, oxidation, ageing, weather, aggressive chemicals and high temperatures.[4,5]

An analytical characterization is necessary for both, the development of new types of propylene based polymers as well as their large scale production. Crystallization based analytical techniques are currently used to analyze PP[6-21], EP[11,12,15,22-31], EPDM[22,32], PP-HI[3,20,33-42] and other propylene based polymers with regard to their chemical heterogeneity.[43] These include Crystallization Analysis Fractionation (CRYSTAF)[44], Temperature Rising Elution Fractionation (TREF)[45] and Crystallization Elution Fractionation (CEF).[46] All of them exploit the fact that the crystallization temperature of macromolecules from dilute solution depends on their comonomer content and their stereo- and regio-microstructure.[47] However, crystallization based techniques do not separate amorphous polymers selectively, and interpreting the results may be complicated by effects of co-crystallization or molar mass.[48] The effect of co-crystallization has been studied for binary blends of PP and propylene based copolymers using Differential Scanning Calorimetry (DSC).[49] It was observed that co-crystallization becomes significant with increasing ethylene content in the propylene based copolymer.

Chromatographic analytical techniques e.g., High Temperature Size Exclusion Chromatography (HT-SEC) has been used for decades to determine the Molar Mass Distribution (MMD) of polyolefins.[50] SEC is an entropy driven process i.e., the macromolecules are separated according to their hydrodynamic volume in the solution and do not interact with the stationary phase. High-Temperature Liquid Adsorption Chromatography (HT-LAC) has recently emerged as an alternative technique to determine the Chemical Composition Distribution (CCD) of polyolefins. HT-LAC, based on selective adsorption of polyolefins from specific mobile phases onto Porous Graphitic Carbon (PGC), was for the first time described by Macko et

al.[7,43,51,52] LAC is an enthalpy driven process i.e., the macromolecules are separated due to their selective adsorption on the stationary phase, and then following desorption at a particular mobile phase composition and temperature.[53,54] In between these two chromatographic modes, a third mode exists which is referred to as Liquid Chromatography at Critical Conditions (LCCC). LCCC is found at the transition from SEC to LAC (SEC → LCCC → LAC), where entropic effects of separation are equivalent to enthalpic effects. LCCC is from a practical point of view important because it enables to achieve separations, which are not realizable with other chromatographic methods. For example, LCCC has been applied to block copolymers[55-63] to determine the average molar mass and the MMD of constituent blocks in di- and tri-block copolymers (type A–B and A–B–A).[64,65] Another unique capability of LCCC is to selectively separate end-functionalized polymers according to their functional groups.[55,66-68] Several groups have described successful separations of macromolecules according to their architecture (for example, linear from star shaped or linear from rings)[69-72] or their tacticity[53,54,73-76] with LCCC.

High Performance Liquid Chromatography (HPLC) is according to IUPAC nomenclature[77] the general term used for the liquid chromatographic techniques (i.e., SEC and LAC) and, in the case of polymers also comprising LCCC. Deviating from that the acronym HPLC has recently been used synonymously in the literature for the LAC mode of liquid chromatography. The abbreviations SGIC and TGIC have been added, describing Solvent Gradient Interaction Chromatography and Temperature Gradient Interaction Chromatography as variants. Chromatographic separations with regard to individual molecular metrics can be hyphenated to study

the correlation between these, yielding the corresponding multivariate distribution. The hyphenation of HT-LAC with HT-SEC (HT-LAC x HT-SEC) is also referred to as High Temperature Two Dimensional Liquid Chromatography (HT 2D-LC) and it has in recent times been used to characterize various polyolefins.[12,32,42,54,78-80]

The aim of the work presented in this thesis is to develop experimental protocols for HT-LAC and HT 2D-LC of PP and propylene based copolymers. The types of PP, propylene based copolymers and the techniques used for their characterization will be elaborately discussed. Critical conditions in various mobile phases will be identified for the stereochemical variants of PP. Procedures to interpret data from HT 2D-LC with Infra-Red (IR) detection (HT 2D-LC-IR) in a quantitative manner will be developed. New sorbents will be probed with regard to their potential as stationary phase for the separation of polyolefins.

# 3 Theoretical background

## 3.1 Polypropylenes and propylene based copolymers

The global demand for polyolefins is expected to reach 200 million tons by 2020 and most of it is predicted to be PP. 82 million tons of PP is expected to be produced by 2020. A forecast for the demand of PE and PP is shown in Figure 1.

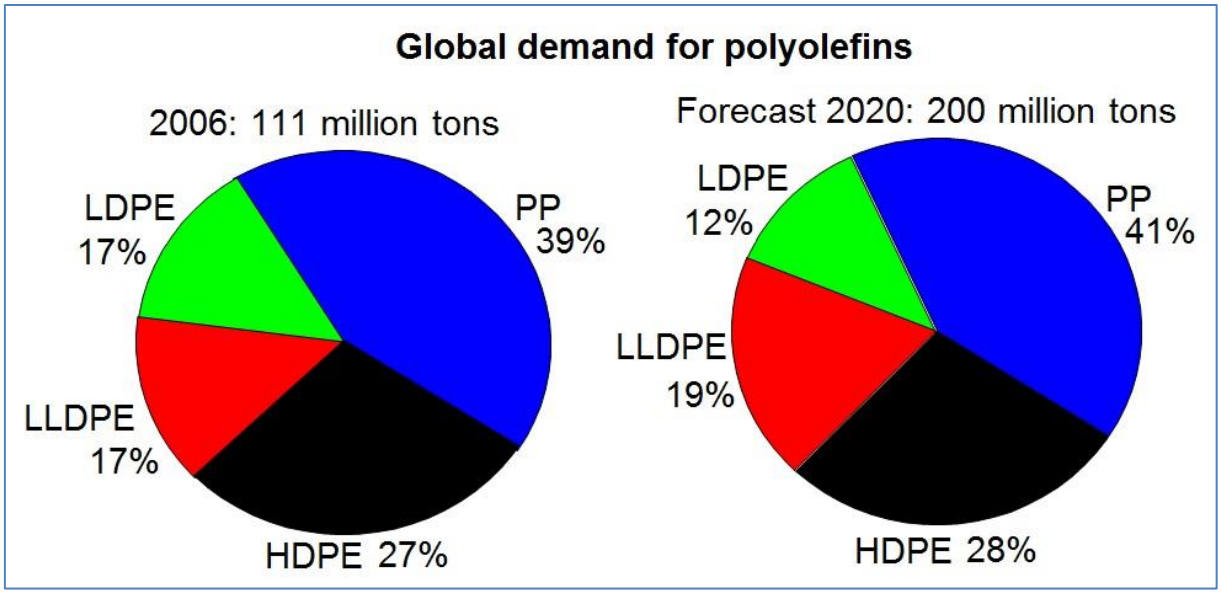



*Figure 1. Global demand for PE and PP.[81]*

### 3.1.1 Polypropylene

PP was first synthesized by Natta, following the discovery of Ziegler, by transition metal catalyzed polymerization of propylene in 1954.[82,83] The main molecular metrics that influence the macroscopic properties of the homopolymer are stereo-regularity of the monomer linkage (tacticity), the MMD and the corresponding average molar mass. There are three steric arrangements of the methyl groups linked to every second carbon atom in the chain: In the isotactic form the methyl groups are placed on the same side of the backbone while in the syndiotactic variant the methyl

groups are placed on alternating sides. The structure where the methyl groups point in a random manner from the polymer backbone is the atactic form. Figure 2 depicts the stereochemical configurations of PP.

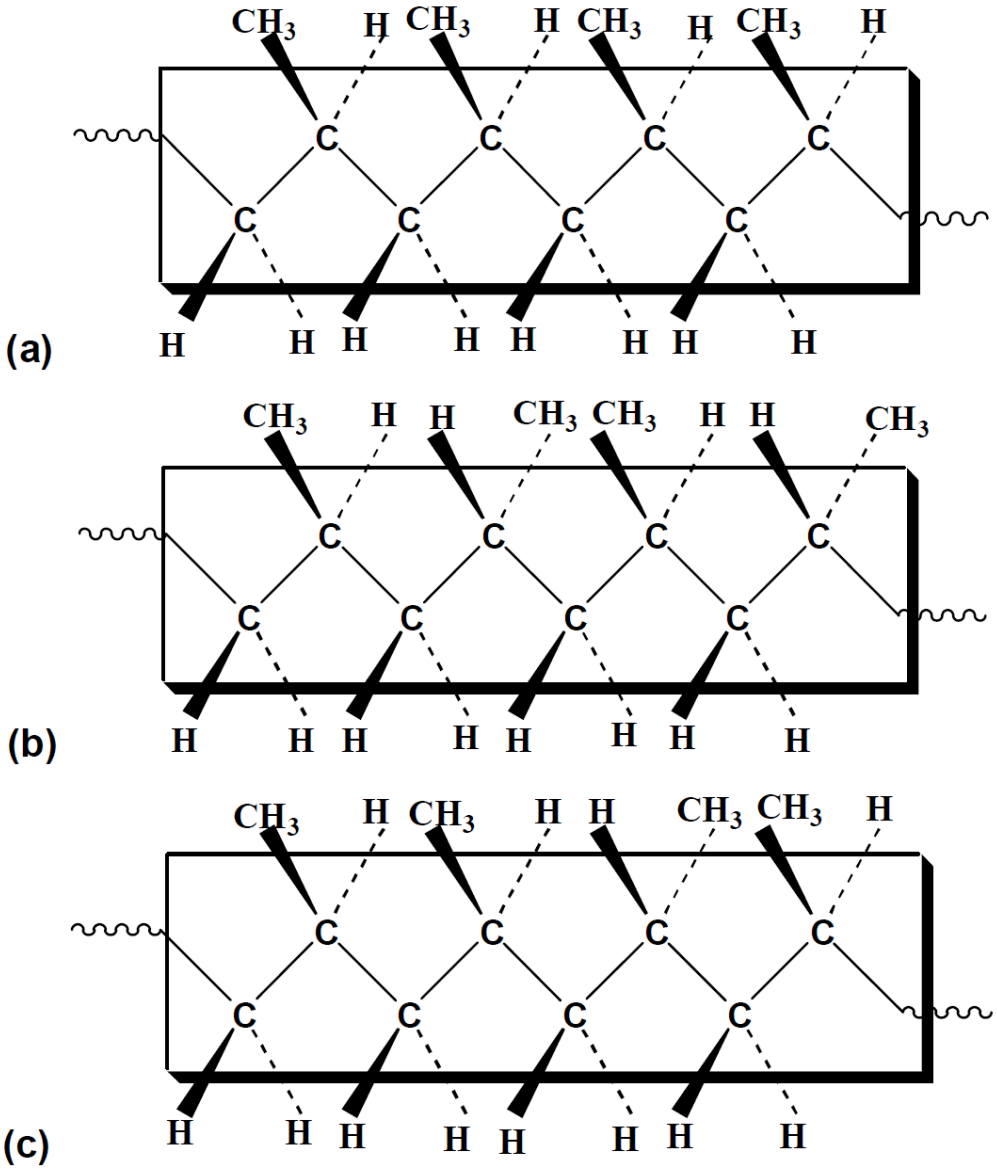



*Figure 2. Stereochemical configurations of PP: a) it-PP, b) st-PP and c) at-PP.*

Atactic polypropylene (*at*-PP) was the only form available before the discovery of stereospecific Ziegler-Natta catalysts. *it*-PP is a relatively low cost material, especially on a volume basis, and due to its inherent low density and superior mechanical

properties attractive for many applications in packaging, transport, appliances, furniture, and textile. It has a relatively lower density (0.905 g/ml), a high melting temperature (≈165 °C), and improved tensile strength compared to PE. Yet, at the same time the impact strength is low. Syndiotactic polypropylene (*st*-PP) was developed more recently. It is the advent of Metallocene catalysts which enabled a commercially viable route for *st*-PP. Compared to *it*-PP; *st*-PP exhibits a lower melting point (130 °C), lower stiffness, slower crystallization, and improved clarity and impact properties. Higher stiffness at a lower density (0.89 g/ml) and better resistance to higher temperatures when not subjected to mechanical stress (particularly in comparison to HDPE and LDPE) are the key advantages of *st*-PP over many other polymers for several applications. In addition to this *st*-PP offers good resistance towards fatigue and Environmental Stress Cracking (ESCR) and is relatively inert towards aggressive chemicals. Comparisons between the density and the melting points of PP's and PE's are shown in Figure 3.

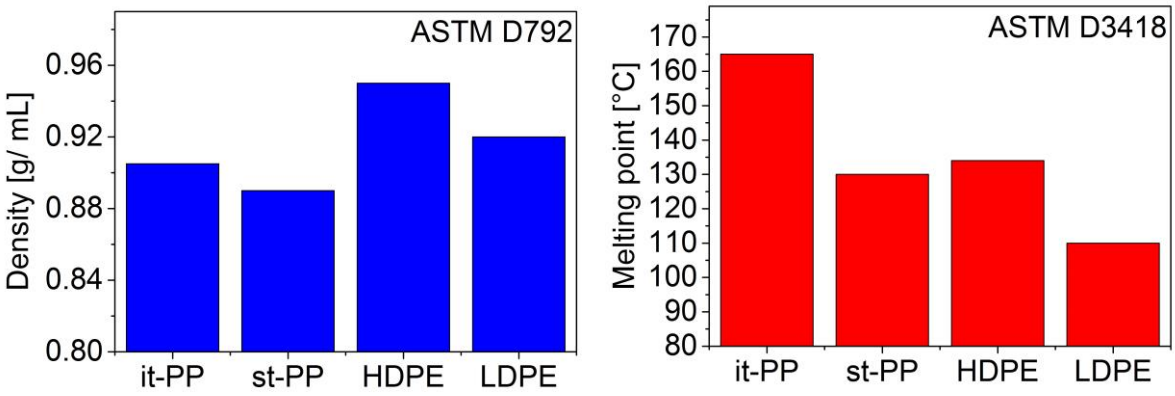



*Figure 3. Comparison of density and melting points of PP's and PE's.*

### 3.1.2 Propylene based copolymers

The copolymerization of propylene with other comonomers may lead to a range of commercially relevant products. Propylene random copolymers (PP-R) are produced by polymerizing propylene with ethylene or 1-butene (up to 5 wt. %). Increasing the ethylene content leads to rubbery products, referred to as EP rubbers. The crystallizability of EP copolymers as well as the melting temperature as function of composition follows a U-shaped trough as shown in Figure 4.[21]

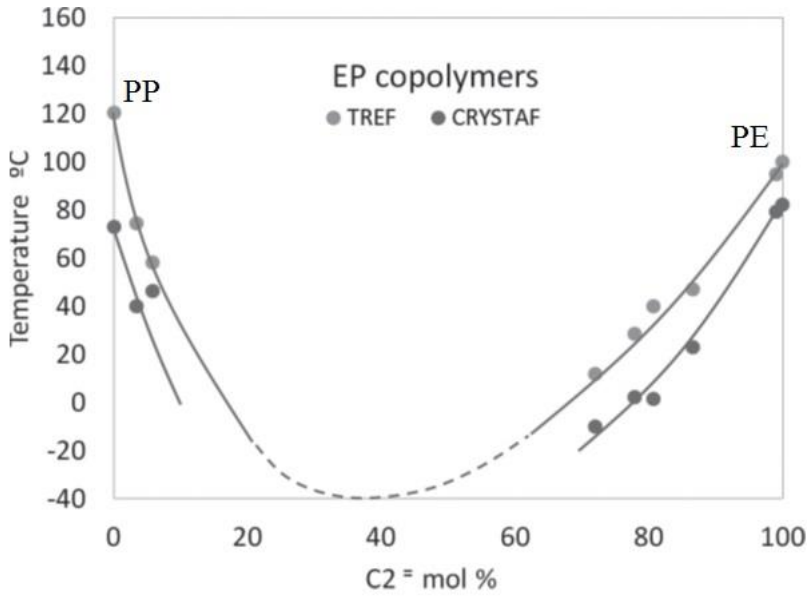



*Figure 4. Elution temperatures of EP copolymers varying with ethylene content.[21]*

The incorporation of ethylene in EP copolymers leads to different products according to their crystallinity (e.g., semi-crystalline PP-R and amorphous EP rubbers). The elastic modulus of EP copolymers can be increased by crosslinking them.[84] EP copolymers display excellent non-conductivity for electricity and, being fully saturated, resistance to ozone. As a result they are confectioned into products for use in automotive engines, electrical wiring and construction.

Propylene is also used to produce terpolymers. Ethylene-Propylene-Diene-Monomer (EPDM) is the commonly produced terpolymer of propylene, which is also referred to as EPDM rubber. EPDM rubbers may contain varying amounts of ethylene, propylene and diene monomers according to their commercial applications. Propylene terpolymers with high levels of ENB are particularly suitable for the production of profiles by pressure-less continuous vulcanization, or for co-vulcanization with diene rubbers.[85]

### 3.1.3 PP-HI

One way to overcome the low impact resistance of *it*-PP is to copolymerize propylene with a small amount (0.5 – 5 wt. %) of ethylene, yielding PP-R. An alternative approach, which has received particular attention in the past decade, is high impact PP (PP-HI). PP-HI is produced using at least two reactors in series with heterogeneous Ziegler–Natta or supported Metallocene catalysts.[83,86] The first reactor is used to produce *it*-PP (semi-crystalline phase), while in the second reactor a fraction of amorphous copolymer (rubber phase) is produced by adding ethylene. The rubber phase is usually an EP rubber, although EPDM can also be used.[87] Due to the consecutive synthesis the amorphous copolymer is finely dispersed in the homopolymer phase, even though the two phases are thermodynamically immiscible. The copolymer phase dissipates mechanical energy during impact and thereby greatly increases the impact resistance of the semi-crystalline polymer. Various molecular parameters influence the performance of PP-HI, including the amount of elastomer and the size distribution of the rubber particles, which in turn is a function of the CCD and the MMD, in particular of the elastomer.[87]

## 3.2 Characterization techniques

Crystallization based and liquid chromatographic analytical techniques are widely used to determine the distribution of molecular heterogeneities (e.g., CCD, MMD) in polymers. The use of these analytical techniques will be discussed in the subsequent subchapters.

### 3.2.1 TREF, CRYSTAF and CEF

The crystallization based techniques for the analysis of CCD of polyolefins may be divided according to their chronology of development into – Temperature Rising Elution Fractionation (TREF), Crystallization Analysis Fractionation (CRYSTAF) and Crystallization Elution Fractionation (CEF).

TREF was first reported by Desreux and Spiegels in 1950[88] and has been applied as a routine method to determine the CCD of polyolefins since the late 1980s.[89] The separation in TREF is based on a two-step process of crystallization and dissolution→elution. The sample is dissolved in a thermodynamically good solvent and loaded into a column packed with an inert support (e.g., glass beads) at elevated temperatures. The loaded column is then cooled at a constant rate with no solvent flow, whereby the macromolecules are fractionated according to differences in their crystallization temperature from the solution. In the next step the crystallized sample is re-dissolved by increasing the temperature, and eluted in a constant flow of the solvent. The macromolecules elute at different temperatures. These fractions can be either collected for further off-line characterization (pTREF) or analyzed on-line with the help of a concentration-sensitive detector e.g., infra-red (IR) detector (aTREF). Crystallization is the most important step in TREF, and the cooling rate has been

observed to have a strong influence on the quality of the separation with lower cooling rates resulting in a higher resolution.[90] The type of support has little to no influence on the fractionation process, and glass beads and stainless steel shots are commonly used for this purpose. The solvent of choice for TREF of polyolefins are xylene, ODCB and TCB.

Monrabal et al.[91] experimentally established a linear correlation between the temperature of elution and the SCB content in TREF separations of LLDPE. However, separations from TREF suffer from limitations with respect to throughput and long duration of experiments, which has led to the development of other techniques. Soares et al.[90] explained the broadening of the peaks in TREF observed with increasing comonomer content on the basis of Stockmayer's bivariate distribution.

In this sense CRYSTAF was developed which uses a single crystallization step without the elution step common to TREF.[44] An aspect of practical relevance is the fact that 5 samples could be analyzed simultaneously which speeded up the characterization process. In CRYSTAF the polymer is dissolved in a thermodynamically good solvent (e.g., ODCB, TCB) at elevated temperatures inside a cylindrical reactor. Aliquots of the polymer solution are filtered out and analyzed with a concentration sensitive detector e.g., IR. The baseline is set from experimental data points taken above the crystallization temperatures. As the temperature is lowered at a fixed rate the polymer sample crystallizes out of the solution according to differences in their crystallizability or SCB/comonomer content. The portion of the sample that remains soluble even at room temperatures (30 °C) i.e., the Soluble Fraction (SF) represents the non-crystalline (amorphous) fraction of the sample.

Brüll et al. showed the separations by CRYSTAF to be independent of the length of comonomer unit for a range of propylene/1-olefin[92] and ethylene/α-olefin[93] statistical copolymers, varying in the type of α-olefins (1-octene, 1-decene, 1-tetradecene, and 1-octadecene). Sarzotti et al.[94] reported that $M_w$ influences on the crystallization temperature in CRYSTAF disappeared above a value of 10,000 g/mol for statistical ethylene/1-hexene copolymers. Analogous to TREF, the peaks in CRYSTAF also exhibit broadening with increasing comonomer content as explained theoretically with the help of Stockmayer's distribution.[95] CRYSTAF has also been applied to separate blends of HDPE/LDPE[96] and PE/PP.[21,96,97] CRYSTAF separations show a linear correlation between the crystallization temperature and the comonomer content of LLDPE[91] similar to TREF. However, although both TREF and CRYSTAF are based on the principle of crystallization TREF has been established to show better resolution as compared to CRYSTAF.[98] Thus, a necessity existed for a method which shows similar resolution as TREF and at the same time overcomes the bottleneck of long analysis time. This led to the development of CEF.

CEF achieves resolution comparable to TREF and enables faster analysis by applying the concept of dynamic crystallization. In dynamic crystallization the different components of a sample are separated from each other in the crystallization step, during which a very slow flow of solvent is maintained.[46] This necessitates the usage of longer columns in CEF and also to optimize the flow rate for achieving the best separation. The application of dynamic crystallization enables the use of higher cooling rates which is the principle reason for faster analysis by CEF compared to TREF and CRYSTAF. Monrabal et al.[17,20,46,99] compared the CC based

characterization of polyolefins by CEF with that by adsorption based technique HT-LAC and Temperature Gradient Interaction Chromatography (TGIC).

### 3.2.2 SEC

The basic assumption in any chromatographic theory is that the retention is controlled by thermodynamic factors.[100,101] In this way, the mobile and stationary phases are considered as thermodynamic phases with volumes $V_{mob}$ and $V_{stat,}$ respectively, and the retention volume $V_R$ at isocratic conditions depends on the distribution (partition) coefficient $k$ of the solute at equilibrium between these two phases:

$$V_R = V_{mob} + kV_{stat} \quad (1)$$

k is related to the standard Gibbs free energy change ($\Delta G_0$), and the latter can be further divided into the enthalpic and entropic contributions of the partitioning process:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = -RT \ln k \quad (2)$$

$$k = \exp(\Delta S^0 / R - \Delta H^0 / RT) \quad (3)$$

Enthalpic interactions and entropic transformations of the solute molecules occur during the chromatographic retention inside the porous stationary phase (Figure 5). When the macromolecule enters the pore it becomes confined and, therefore, cannot assume all possible conformations, which leads to a loss in conformational entropy. At the same time, while being at the surface of the stationary phase, the macromolecule may interact with it, resulting in a change in $\Delta G_0$. When the retention is controlled by

entropic transformations the size exclusion mode is prevailing, while when the retention is ruled by enthalpic interactions, the adsorption mode is at action.

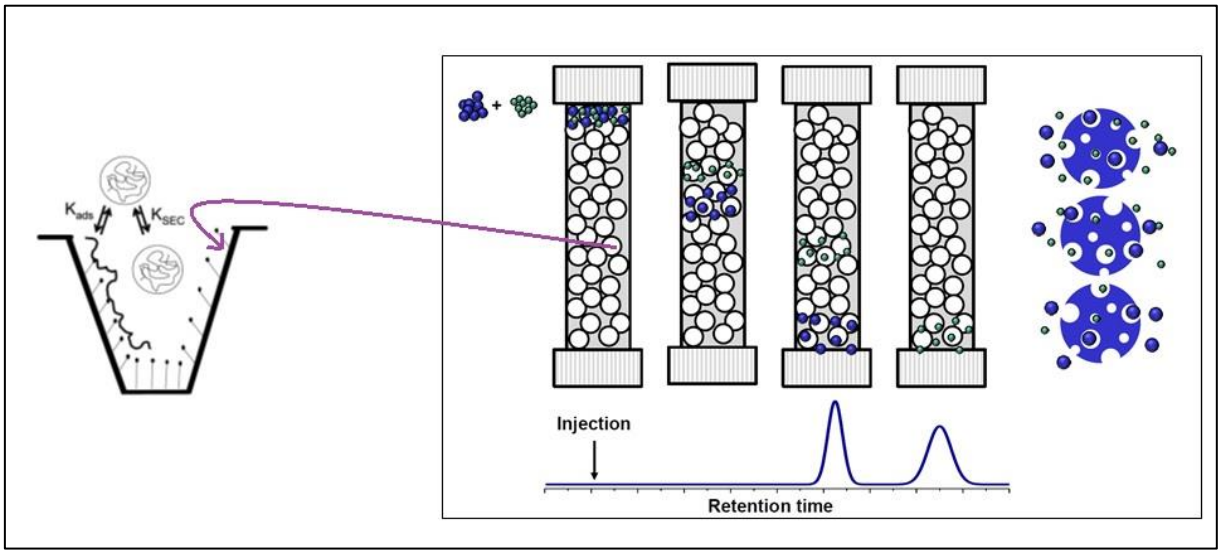



*Figure 5. Schematic representation of the behavior of a polymer molecule in a pore.* ***[102]***

SEC has been used for decades to determine the MMD of polymeric materials. SEC of PP and propylene based copolymers of semi-crystalline nature requires elevated temperatures as these polymers are not soluble at room temperature. SEC performed at elevated temperature is also referred to as HT-SEC.

As has been pointed out, SEC is entropy controlled and the separation is based on differences in the size of the macromolecules in solution (hydrodynamic volume) and the extent to which they are excluded from the pores of a porous column packing. The parameter, which determines the separation i.e., the hydrodynamic volume, is a function of the molar mass, the chain architecture and the chemical composition. In ideal SEC the separation is exclusively ruled by conformational changes of the macromolecules, while the enthalpic interactions are suppressed ($\Delta H^0 = 0$), thus:

$$k = k_{SEC} = \exp(\Delta S^0 / R) \quad (4)$$

SEC is a well-established method to determine the MMD of polyolefins[103] and requires in the case of semi-crystalline polyolefins temperatures above 100 °C. Cross-linked Poly (Styrene-Divinylbenzene) (PS-DVB) gel with varying pore size distribution is used as stationary phase and thermodynamically good solvents suppressing enthalpic interactions, normally 1,2,4-trichlorobenzene (TCB) or 1,2-dichlorobenzene (ODCB).[103]

To characterize the MMD the corresponding number average molar mass, $M_n$, and the weight average molar mass, $M_w$ are widely used.[101] $M_n$ corresponds to the ordinary arithmetic average molar mass of the chains of a sample (Equation 5), whereas $M_w$ (Equation 6) is the average molar mass of a chain in which a monomer has the highest probability to be found. The broadness of the MMD is usually characterized by the dispersity, Đ, calculated by dividing $M_w$ by $M_n$. Since per definition $M_w$ is equal or higher than $M_n$, Đ is always > 1 and the higher Đ the broader the MMD. Equations to calculate both average molar masses and Đ are:

$$\overline{M}_n = \frac{\sum_i N_i M_i}{N_i} \quad (5)$$

$$\overline{M}_w = \frac{\sum_i N_i M_i^2}{N_i} \quad (6)$$

$$Đ = \frac{\overline{M}_w}{\overline{M}_n} \geq 1 \quad (7)$$

A refractive index (RI) detector is commonly used to monitor the concentration of polymer eluting from the columns (SEC/RI). More recently, infrared (IR) detection

has gained popularity as concentration sensitive detector for SEC (SEC/IR). The main advantages over the more traditionally used RI detectors are increased baseline stability and lower sensitivity towards temperature fluctuations in the detector cell. Additionally, IR detectors can deliver information about the chemical composition of the eluting fractions. If the polymer chains are linear, a direct relationship exists between the molar mass volume in solution and elution time for a given polymer type. This is used to create a calibration curve relating the elution time (volume) to the molar mass. In addition, a universal calibration curve (obtained using Polystyrene (PS) standards i.e., molar mass of PS standards vs. elution volume from SEC) can be used to extend this relation to linear polymers of all types, provided that the relation between intrinsic viscosity and molar mass of the polymer is known (using, for instance, the Mark–Houwink equation) or measured by an on-line viscometer (SEC/RI-VISC).

SEC-FTIR of polyolefins is typically performed in two ways: either the eluent from the SEC column is sprayed onto a rotating germanium disk and subsequently analyzed off-line by FTIR[104] or the SEC is coupled to a heated flow cell placed in an FTIR spectrometer.[105,106] Hereby profiles are obtained showing the MMD and, additionally, the content of SCB or other comonomer-units of interest as a function of molar mass. Nowadays, besides IR spectrometers recording full spectra, IR detectors with fixed wavelengths using at least two different band pass filters are also available for compositional analysis.[107] TCB, ODCB or Tetrachloroethylene can be used as mobile phase for flow-through FTIR detection as it is sufficiently transparent in the spectral window 3500 - 2700 $cm^{-1}$, which corresponds to the >C-H stretching region i.e., the region of interest for polyolefins. Typically, at least two bands associated to

methyl (-$CH_3$) and methylene (-$CH_2$) groups are measured and their ratio is calibrated against polymer standards (ratio method).[24,107] This procedure is simple to apply and usually appropriate for samples having a medium to high degree of SCB. Very low degrees of branching (<2 -$CH_3$/1000C) pose a limit due to the signal-to-noise ratio.

In sum, SEC separates macromolecules according to their size in solution. Macromolecules of the same size (hydrodynamic volume), however, may differ in their chemical composition. FTIR-spectroscopy enables to evaluate the average chemical composition of fractions eluting from SEC but a distinction of macromolecules according to their chemical composition in individual SEC slices i.e., their chemical heterogeneity, is not possible in that way.

### 3.2.3 LAC

LAC has been widely used to separate polymers with respect to their chemical composition. The majority of published LAC separations of synthetic polymers has been realized at temperatures below 60 °C.[101,108] Dissolution and chromatographic separation of semi-crystalline polyolefins, however, require temperatures of up to 160 °C.[109-111] Consequently the separations are referred to as HT-LAC.

The industrial production of polyolefins started in England in 1939.[112] Yet, HT-LAC methods to separate polyolefin materials according to their chemical composition, however, were not available for a long time for two reasons:

- Stationary phases which adsorb polyolefins were not known.
- A dedicated HT-LAC instrument was not available in the market.

Strong retention of linear PE and *it*-PP from dilute solutions in decalin on specific zeolites was observed by Macko et al. in 2003.[109-111,113] Unfortunately, the adsorption was irreversible, and thus, the polymer could not be recovered. The first chromatographic systems for the separation of polyolefins according to their chemical composition (HT-LAC) were published only recently.[114-116] They were based either on the selective precipitation/dissolution (PP is soluble in ethylene glycol monobutyl ether while PE non-soluble) or on the selective adsorption/desorption of PE or PP.[117-119]

The first sorbent-solvent system for HT-LAC of non-polar polyolefins was published by Macko and Pasch in 2009.[7] The authors described the chromatographic separation of PE from PP as well as the separation of PP according to tacticity.[7] In detail it was shown that *at*-PP, *st*-PP and linear PE could be adsorbed on the surface of PGC from 1-decanol as mobile phase, while *it*-PP eluted without any retention. The retained polymers were desorbed by applying a linear solvent gradient 1-decanol→TCB. The technological superiority of the liquid chromatographic approach stems from the fact that the separation is independent from the crystallizability of a sample. Thus, for the first time also amorphous materials can be separated. An advantage from the practical point of view is that crystallization based techniques require larger amounts of samples, solvents, and time. It was demonstrated that HT-LAC enables to separate EP copolymers over the full range of ethylene content.[22,23]

The applications of HT-LAC for the separation of polyolefins have been thoroughly reviewed by Macko et. al.[8] It was shown that EVA[120-122], EMMA[122,123], as well as EMA copolymers[122,123] can be separated with regard to their chemical composition. The separations were based on a full adsorption of macromolecules from

specific solvents (e.g., decalin or TCB) on bare silica as stationary phase at 140 °C and a subsequent desorption controlled by adding cyclohexanone to the mobile phase. Parallel to the systems that separate non-functionalized polyolefins, the first chromatographic systems which can separate functionalized polyolefins (PP-g-MA)[124] according to chemical composition at high temperature were developed. Nagar et al.[124] have applied silica gel and Mica as stationary phases and a solvent gradient decalin → cyclohexanone for the separation of PP-g-MA at 140 °C using HT-LAC.

### 3.2.4 LCCC

LAC is an enthalpy driven process i.e., the macromolecules are separated due to their selective adsorption on the stationary phase, and then following desorption at a particular mobile phase composition and temperature.[53,54] SEC is an entropy driven process i.e., the macromolecules are separated according to their hydrodynamic volume in the solution. In between these two chromatographic modes of separations, a third mode (LCCC)) exists at the transition from SEC to LAC (Figure 6).

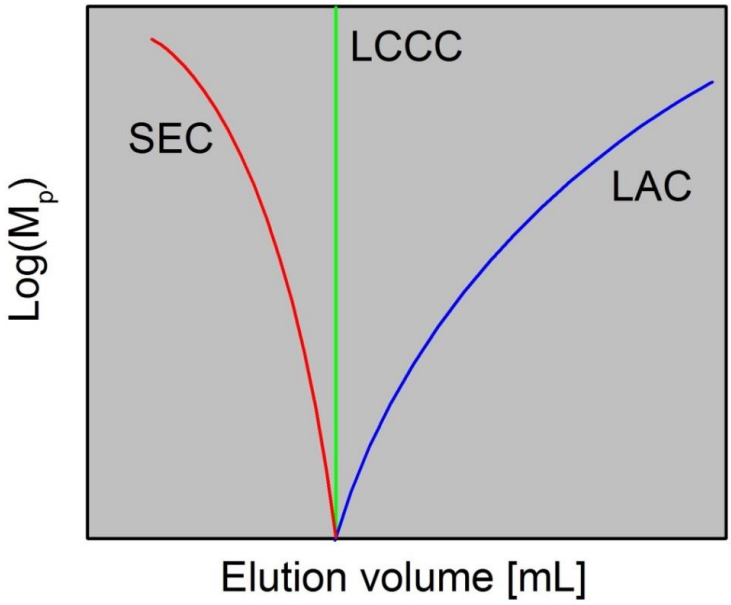



*Figure 6. Relation between the molar mass and the elution volume in different separation modes of liquid chromatography.*

LCCC is for a given combination of polymer/stationary phase/mobile phase at a specific temperature observed when the entropic term completely equals the enthalpic contributions i.e., $\Delta G = 0$. In LCCC the macromolecules with identical repeating units elute independent of their $M_W$, and their elution behavior is determined by subtle compositional or structural differences. The existence of LCCC was first theoretically postulated by Belenkii et al.[125] and Entelis et al.[66] Since then, LCCC has been applied for:

a) Separation of block copolymer[55,56,58-63]
b) Determining the $M_W$ of constituent blocks in di- and tri-block copolymers[64,65]
c) Separation of end-functionalized polymers based on the type of functional group[55,66-68]

d) Separation of polymers based on their architecture (for example, linear from star shaped, or linear from rings)[69-72]

e) Separations based on tacticity[73-76]

As of 2003 more than 250 chromatographic systems for LCCC were known at ambient temperatures and their applications were reported.[126]

As conditions for LAC of polyolefins were not known until recently, LCCC separations were limited to those olefin di-block copolymers for which critical conditions of the non-olefinic segment were known i.e., polystyrene in styrene/ethylene copolymers,[65] and poly methyl methacrylate, PMMA, in MMA/ethylene copolymers.[127]

### 3.2.5 2D-LC

SEC, which provides information about the MMD of polymers and LAC, which delivers information about the CCD of polymers can be hyphenated to provide the bivariate distribution (MMD x CCD) of a polymer. The bivariate distribution in a polymer sample and their separation are shown in (Figure 7).

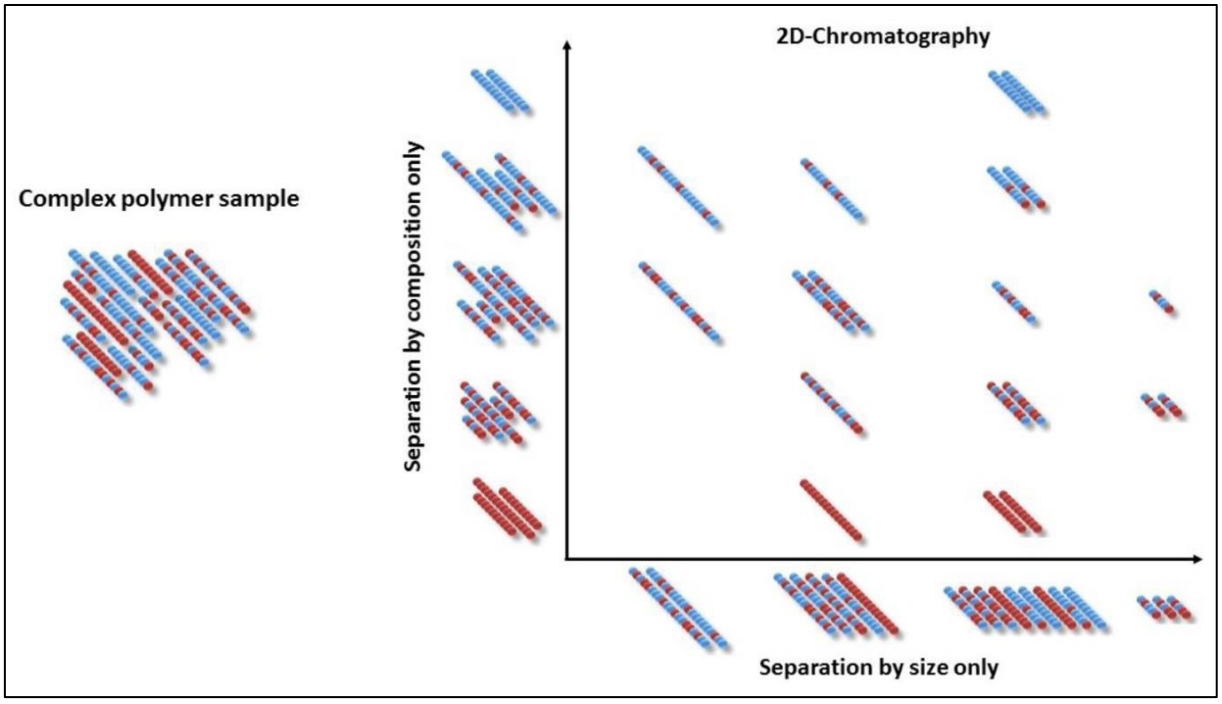



*Figure 7. Principle of 2D separation. The red spheres in the figure represent unit A and the blue spheres represent unit B.*

As discussed, polyolefins are distributed with regard to more than one parameter. It is obvious that *n* independent parameters require *n*-dimensional analytical methods for independent characterization of the different structural parameters. This principle of "orthogonal chromatography" was suggested by Balke and Patel.[128,129] In practice, however, this is not easy to realize: SEC for instance is always affected by differences of the macromolecules in their chemical composition since the

hydrodynamic volume is also a function of chemical composition, and vice versa LAC suffers from molar mass effects. Nevertheless, two- and multi-dimensional separations have become indispensable for the separation of polymers with multivariate heterogeneities.

2D-LC implemented by coupling two separations exists in three modes: on-line; stop-and-flow; and off-line. Each approach has distinct features and drawbacks; particular approaches allow making use of one of them more advantageous than that of the other ones for some specific applications, as it was demonstrated by Fairchild et al.[130] The resulting data is a matrix, usually represented as a contour plot, with each chromatographic separation along an axis.

The sequence of separation method is an important aspect in achieving the best resolution and most accurate determination of distributions. It is advisable to use the method with the highest selectivity for the separation of one distribution as the first dimension. This ensures highest purity of eluting fractions being transferred into the subsequent separation.[131] The advantages and disadvantages of using either LAC × SEC or SEC × LAC sequences were discussed in detail by van der Horst and Schoenmakers.[132,133]

In the very first examples of 2D-LC separations of synthetic polymers (e.g., PS), SEC was performed first[134] followed by LAC in the second dimension.[128,129] The first dimension was operated with THF as the eluent, whereas for second dimension gradients of THF-heptane were used. In the case of using SEC in the first dimension, each fraction is dissolved in a thermodynamically good solvent and breakthrough peaks can occur when these fractions are further injected into a LAC column.[135]

It seems to be more advantageous to use a sequence of methods, in which the first dimension separates according to chemical composition. In this way information on the CCD can be obtained and the fractions eluting from the first dimension can then be analyzed independently in SEC mode in the second dimension to retrieve the required MMD information. In such cases SEC separates strictly according to molar mass, and the information thus obtained is quantitative.[131]

Apart from the consideration of selectivity, the choice of detectors is an important aspect when hyphenating two separations: For the case of LAC, Evaporative Light Scattering (ELS) detection is widely used to monitor the effluent as it offers the advantage that the solvents of a mixed mobile phase are evaporated and thus not detected, while polymers are.[9,10,12,20,43,53,54,80,136-139] The response of the ELS detector, however, may depend on several parameters, including the nature and composition of the mobile phase as well as that of the polymer, and it is non-linear with respect to the concentration of the polymer.[140] These shortcomings severely limit the use of an ELS detector for quantitative analysis.

As the elution in SEC occurs isocratic, Refractive Index (RI) and UV detectors are widely used to obtain quantitative information for a wide range of polymers soluble at room temperature. In the case of HT-SEC the use of aromatic solvents as mobile phase prevents the use of UV detection. Instead, filter based IR detection has been extensively used for quantitative analysis with HT-SEC,[50] as well as for crystallization based techniques like CRYSTAF,[44] TREF[45] and CEF[46] as its response varies linearly with the concentration of an analyte. Monitoring the eluent from the 2$^{nd}$ dimension of HT 2D-LC by filter based IR-detection has opened a new window for the quantitative analysis of the polyolefins.[141]

Generally, the detection principles of SEC can be applied to the corresponding two dimensional separations, and thus, the LAC x SEC hyphenation offers more flexibility regarding the detection. Yet, it has to be kept in mind that the solvent used in the first dimensional separation usually contains aliphatic protons i.e., it is detected by the filter based IR-detector. The chromatographic conditions in HT 2D-LC have thus to be optimized in a way that the solvent peak does not interfere with the peak corresponding to the eluting fractions of a polymer analyte.

In most of the cases, the results from 2D-LC have been presented as contour plots and compared qualitatively.[12,32,78,79,142] The relative volume of spots in different contour plots was compared to derive quantitative information about constituents of samples,[54] yet this procedure does not provide quantitative information about segments, which are present in both samples (i.e., species having either identical molar mass and chemical composition), and segments, which are present only in one sample out of compared samples (different or unique segments).

# 4 Experimental part

## 4.1 HT-SEC

A PL GPC 220 (Agilent, Waldbronn, Germany) was used to determine the molar mass distribution from which the corresponding average values were calculated. The temperature of the injection sample block and of the column compartment was set to 150 °C. The flow rate of the mobile phase was 1 mL/min. The polymers were dissolved for 2 h in TCB (Merck, Darmstadt, Germany) (containing 2 g butylated hydroxytoluene/L) at a concentration of ~1 mg/mL at 150 °C. 200 $\mu$L of a polymer solution were injected. Polystyrene standards (Polymer Standards Service, PSS, Mainz, Germany) were used for calibration of a column set (3 x PL gel Olexis columns, Mixed B, 300 x 7.5 mm (L. x I.D.), particle size 13 $\mu$m, Agilent, Waldbronn, Germany). An infrared detector (model IR4, PolymerChar, Valencia, Spain) was used.

## 4.2 HT-LAC

A high temperature liquid chromatograph (PL-XTR 220, Polymer Laboratories, Church Stretton, England) was used for the experiments. The temperatures of the injector, the transfer line, and the column oven were set at 160 °C. The sample loop had a volume of 50 $\mu$L. An Evaporative Light Scattering Detector (ELSD) model PL-ELS 1000 (Polymer Laboratories) was used to monitor the composition of the effluent. Temperatures of the nebulizer and evaporator were fixed at 160 °C and 260 °C, respectively, and a nitrogen flow rate of 1.5 L/min was used for nebulization of the effluent. Data collection (1 point/s) and processing were done with PSS-WinGPC-Unity software (Build 5403) from Polymer Standards Service, Mainz, Germany.

A high-pressure binary gradient pump (model 1100) from Agilent, Heilbronn, Germany was used for mixing and pumping the mobile phases. The mobile phase flow rate was maintained constant at 1 mL/min.

A linear solvent gradient as described in Table 1 was used for all LAC experiments. The last part of the gradient program served to re-establish the original adsorption equilibrium in the column.

*Table 1. Composition of the mobile phase in the gradient pump and in ELSD.*

| **Desorption promoting solvent [vol. %]** | **Linear gradient [min.]** | |
|---|---|---|
| | **In pump** | **In ELSD** |
| 0 | 0 | 0 |
| 0 | 3 | 8.1 |
| 100 | 13 | 18.1 |
| 100 | 17 | 22.1 |
| 0 | 20 | 25.1 |
| 0 | 45 | 50.1 |

The total delay volume of the HT-LAC system was determined according to Ginzburg et al.[142] as 5.1 mL.

### 4.3 HT-LCCC

The instrument used for HT-LAC experiments was also used for HT-LCCC experiments. The program shown in (Figure 8) was applied to check the recovery of polymer, while determining the critical conditions using new method.

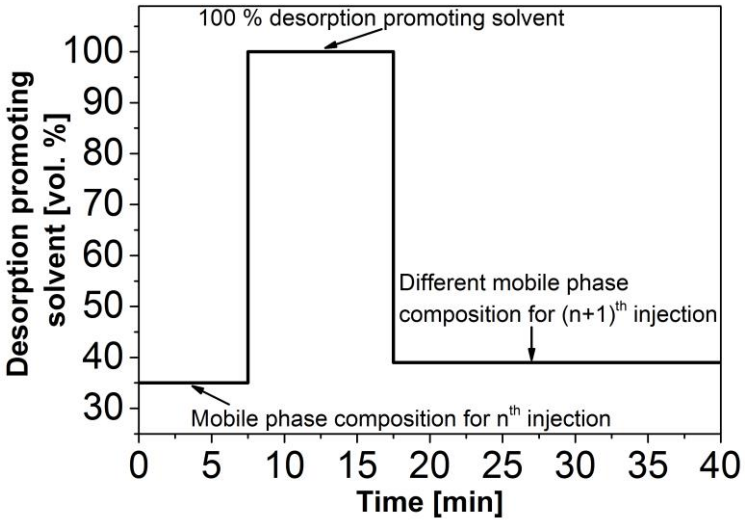



*Figure 8. Composition of the mobile phase for $n^{th}$ and $(n+1)^{th}$ injection versus time.*

The polymer was injected into such a mobile phase composition that the polymer was fully or partially adsorbed in the column. Subsequently, the retained polymer was desorbed and eluted after pumping a desorption promoting solvent (TCB or ODCB). For the next injection the concentration of desorption promoting solvent in the mobile phase was increased, the column was purged for 10 minutes with the new mobile phase and polymer was again injected. This procedure was repeated until no peak of the polymer appeared on the chromatogram after purging the column with TCB or ODCB.

### 4.4 HT 2D-LC

A prototype HT 2D-LC instrument (PolymerChar, Valencia, Spain) was used. The chromatograph was equipped with an autosampler (Agilent) for heating and injecting the samples into the first dimension column. Two separate ovens were used for heating the LAC and SEC columns, capillaries and valves. Two pumps, one binary and another one isocratic, equipped with vacuum degassers (Agilent, Waldbronn, Germany) were used for pumping the solvents in the columns as shown in Figure 9. An electronically controlled 8 port valve (VICI Valco instruments, Houston, Texas, USA) was used for transferring fractions from the first column (LAC) to the second column (SEC). The injection loop (LAC) and the transfer loop (SEC) had a volume of 250 $\mu$L and 100 $\mu$L, respectively. An IR4 detector (PolymerChar, Valencia, Spain) and an ELS detector (PL-ELS 1000 from Polymer Laboratories, Church Stretton, England) were used for monitoring the effluent (Figure 9). The dual wavelength IR4 detector has two filters ($IR_1$ and $IR_2$), which are tuned to specific wavelengths: $IR_1$ monitors the overall concentration of a polymer (i.e., -CH- groups), while $IR_2$ is tuned to measure the presence of methyl ($-CH_3$) groups in a polymer.[143] The ELS detector nebulized the mobile phase at 160 °C in stream of nitrogen with flow rate 1.5 L/min and subsequently the mobile phase was evaporated at 260 °C.

This instrument was modified: Two solvent selector valves, a pump selector and one column selector valve were added, which enabled to select a solvent as well as a column of interest. Moreover, a method selector valve was mounted into the oven (Figure 9), which enabled to realize HT-LAC, HT-SEC and HT 2D-LC measurements in the same instrument.

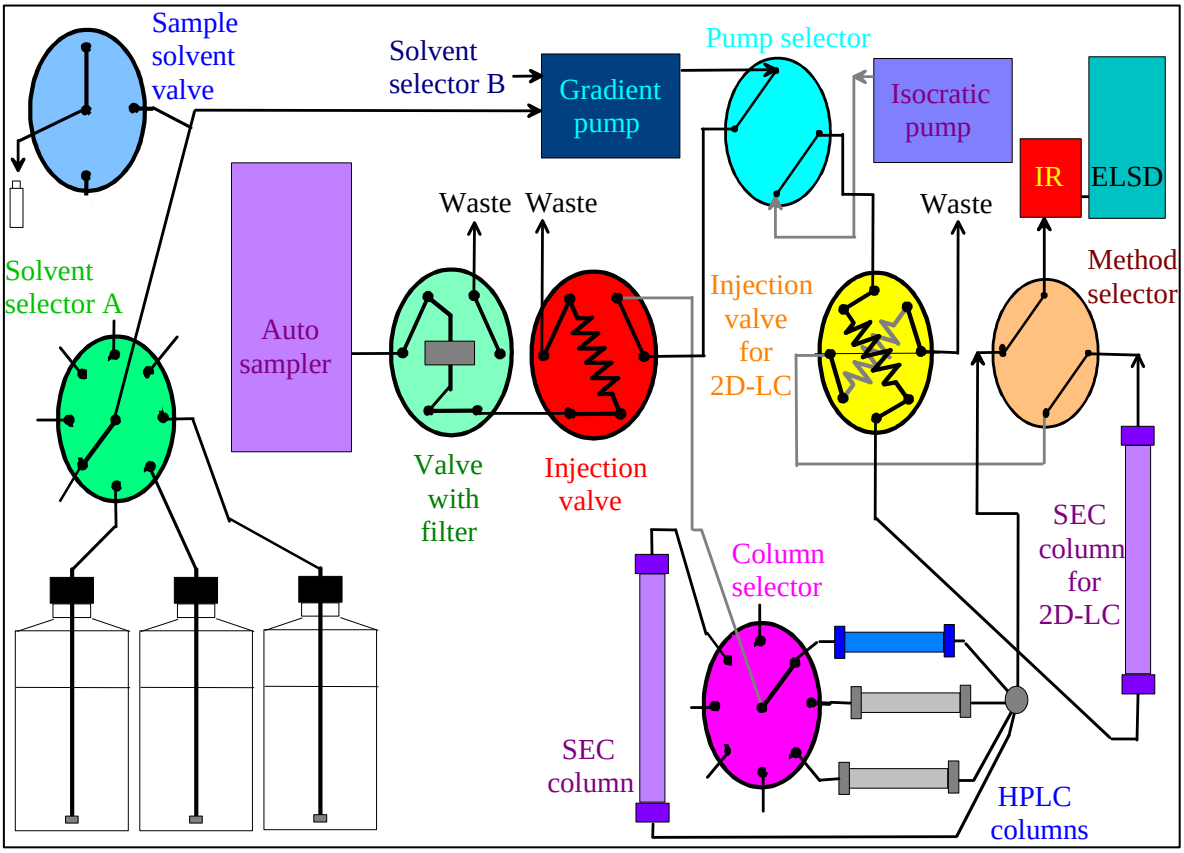



Figure 9. Scheme of the instrument (HT 2D-LC) used for the measurements.

The program for the gradient pump used in HT 2D-LC is included into Table 2.

*Table 2. Composition of the mobile phase in the gradient pump and in ELSD.*

| **Desorption promoting solvent [vol. %]** | **Linear gradient [min]** | | **Linear gradient [mL]** | |
|---|---|---|---|---|
| | **In pump** | **In ELSD** | **In pump** | **In ELSD** |
| 13 | 0 | 0 | 0 | 0 |
| 13 | 100 | 174 | 5 | 8.7 |
| 100 | 120 | 194 | 6 | 9.7 |
| 100 | 200 | 274 | 10 | 13.7 |

| | | | | |
|---|---|---|---|---|
| 13 | 240 | 314 | 12 | 15.7 |
| 13 | 300 | 374 | 15 | 18.7 |

The total delay volume of the HT 2D-LC system was determined according to Ginzburg et al.[142] as 3.7 mL.

The parameters used for the HT 2D-LC measurements are summarized in Table 3.

*Table 3. Parameters of HT 2D-LC measurements.*

| **2D-LC method** | **LAC flow Rate [mL/min]** | **SEC flow Rate [mL/min]** | **Interval Between Two Injections into SEC column [min]** | **Transfer Loop Volume [$\mu$L]** | **Number of Fractions (10 mL Gradient volume)** | **Time for 2D-LC Analysis [min]** |
|---|---|---|---|---|---|---|
| No. 1 | 0.10 | 2.5 | 1 | 100 | 100 | 100 |
| No. 2 | 0.05 | 2.5 | 2 | 100 | 100 | 200 |
| No. 3 | 0.02 | 2.5 | 5 | 100 | 100 | 500 |
| No. 4 | 0.02 | 1.5 | 5 | 100 | 100 | 500 |

The parameters summarized in Table 3 were calculated according to Equations 8 - 10:

$$V_{TL} = F_{LAC}\Delta t \quad (8)$$

$$N_{LAC} = \frac{V_{grad}}{V_{TL}} \quad (9)$$

$$t_{HT2D-LC} = N_{LAC}\Delta t \quad (10)$$

where $V_{TL}$ is the transfer loop volume, $\Delta t$ is the interval between two SEC injections, $F_{LAC}$ is the solvent flow rate in LAC column, $N_{LAC}$ is number of LAC fractions, $V_{grad}$ is volume of the gradient and $t_{HT\ 2D\text{-}LC}$ is time required for one LAC analysis.

The volume of the gradient 1-decanol → TCB (Table 3) was kept constant (10 mL), for the LAC separations.

Data were collected with WinGPC unity software (PSS, Mainz, Germany) and the contour plots and matrices were generated with Origin 9.1 software.

The Standard Deviation (S) in different data sets was calculated using Equation 11 by injecting the samples three times.

$$S = \sqrt{\frac{\sum (Y_i - \mu)^2}{N}} \quad (11)$$

where $Y_i$ is the value of $i^{th}$ data in full data set (i = [*1,2, ….,N*]), $\mu$ is the average of the data set and *N* is the total number of points in the data set.

### 4.5 CRYSTAF

A CRYSTAF apparatus, model 200, manufactured by Polymer Char. S.A. (Valencia, Spain) was used to determine the amount of EP rubber in the PP-HI samples. About

20 mg of the sample were dissolved in 35 mL of distilled ODCB at 160 °C. After the dissolution the temperature of the sample solution was decreased at a rate of 0.1 °C/min between 100 °C and 30 °C. The polymer concentration in solution was monitored with an IR4 detector operating at 150 °C and using 3.5 $\mu$m as the measuring wavelength.

### 4.6 Mobile phases

1,2-dichlorobenzene (ODCB), 1,2,4-trichlorobenzene (TCB), 2-octanol, 2-ethyl-1-hexanol (2E1H), n-decane, diisobutylketone and decalin were obtained from Merck, Darmstadt, Germany. ODCB and TCB were distilled prior to use, the remaining mobile phases were used as received.

### 4.7 Stationary phases

A Hypercarb$^{TM}$ column (4.6 mm x 250 mm ID x L) containing porous graphitic carbon with an average particle diameter of 5 $\mu$m, a surface area of 122 $m^2/g$ and 250 Å pore diameter was purchased from ThermoFisher Scientific, Dreieich, Germany) to use as stationary phase in HT-LAC and HT 2D-LC. A PL Rapide H column (7.5 mm x 150 mm ID x L) from Agilent (Waldbronn, Germany) was used in the second dimension for the separation according to molar mass in HT 2D-LC.

Apart from the commercial columns, 2 manually packed columns obtained from Dr. B. Monrabal (Polymer Char, Valencia, Spain) were tested (Table 4). The data about the average particle diameter, surface area and the pore diameter of these manually packed columns were not provided.

*Table 4. Columns obtained from Dr. B. Monrabal.*

| Stationary phase | Length of the column (mm) | Inner diameter of the column (mm) |
|---|---|---|
| Boron Nitride (BN) | 90 | 7.5 |
| Molybdenum Sulfide ($MoS_2$) | 150 | 7.5 |

## 4.8 Polymer samples

*it*-PP standards were obtained from American Polymer Standards Corporation (Mentor, Ohio, USA). One sample of *st*-PP (*st*-PP$^{196.8}$) and atactic polypropylene (*at*-PP) (*at*-PP$^{45.2}$) was obtained from Sigma-Aldrich (Milwaukee, USA). Several *st*-PP samples were kindly provided by Dr. S. Bo (Chinese Academy of Sciences, Changhun, China). One sample (*at*-PP$^{315}$) was obtained from Dr. I. Mingozzi (LyondellBasell, Ferrara, Italy). High impact polypropylene (PP-HI) samples and EP copolymer samples, which were produced on a laboratory scale, were provided by Dr. K. Remerie (SABIC, Geleen, Netherlands). The PP-HI samples contained 20 and 60 wt. % of ethylene in the EP rubber. Linear PE standards, used for the calibration of SEC axis, were obtained from Polymer Standards Service, Mainz, Germany. These polymer samples were dissolved at 160 °C for 2 hours in the corresponding mobile phase at a concentration of ~2 mg/mL. The molecular characteristics of the polymer samples used are summarized in Table 5.

*Table 5. Weight average molar mass ($M_w$) and dispersity index (DI) of polymer samples.*

| Sample | $M_w$ [kg/mol] | DI |
|---|---|---|

| | | |
|---|---|---|
| *it*-PP$^{1.2}$ | 1.2 | 1.42 |
| *it*-PP$^{8.6}$ | 8.6 | 3.30 |
| *it*-PP$^{52.3}$ | 52.3 | 2.41 |
| *it*-PP$^{95.4}$ | 95.4 | 3.39 |
| *it*-PP$^{136.5}$ | 136.5 | 3.69 |
| *it*-PP$^{231.3}$ | 231.3 | 5.53 |
| *it*-PP$^{348.3}$ | 348.3 | 8.01 |
| *at*-PP$^{14.0}$ | 14.0 | 2.92 |
| *at*-PP$^{45.2}$ | 45.2 | 3.73 |
| *at*-PP$^{315}$ | 315 | 2.60 |
| *st*-PP$^{32.7}$ | 32.7 | 1.22 |
| *st*-PP$^{67}$ | 67 | 1.13 |
| *st*-PP$^{97}$ | 97 | 1.10 |
| *st*-PP$^{134}$ | 134 | 1.10 |
| *st*-PP$^{196.8}$ | 196.8 | 2.44 |
| *st*-PP$^{201}$ | 201 | 1.10 |
| *st*-PP$^{348}$ | 348 | 1.16 |
| PP-HI$_{20}$ | 532 | 9.8 |

| | | |
|---|---|---|
| PP-$HI_{60}$ | 502 | 9.5 |
| $EP_{60/59.7}$ | 125 | 1.9 |
| $EP_{39.8}$ | 125 | 2.7 |
| $EP_{10.4}$ | 165 | 2.1 |
| PE | 2 – 126 | 1.1 – 1.6 |
| $PE^{181}$ | 181 | 1.59 |
| $PE^{84.5}$ | 84.5 | 1.28 |
| $PE^{60}$ | 60 | 1.47 |
| $PE^{36.5}$ | 36.5 | 1.31 |
| $PE^{16.5}$ | 16.5 | 1.37 |
| $PE^{116}$ | 116 | 1.4 |

# 5 Results and discussion

Polypropylene and propylene based copolymers were analyzed to determine their molecular heterogeneities and to identify the correlation between those heterogeneities using various techniques. New stationary phases (similar as Hypercarb$^{TM}$) will be probed with regard to their potential to separate polyolefins via HT-LAC. The obtained results will be discussed in this chapter.

## 5.1 LCCC of PP

In the majority of the papers, the critical conditions are determined by evaluating the dependence between the elution volumes and the molar mass of a series of samples for a polymer of interest (SEC-LAC-plots).[55-76,125] Namely, at a specific composition of a mixed mobile phase and at a given temperature, the polymer samples with different molar mass elute at the same elution volume. This specific composition of the mobile phase is the critical point for the polymer at the applied temperature in this chromatographic system. This method of determining the critical point may be laborious due to the fact that a series of polymer samples with varying molar mass needs to be injected in a mobile phase with varying composition. This may be a particular impediment due to the fact that the required series of polymers are not easily accessible.

Two empirical methods[144,145] have been widely used for rapid identification of the critical conditions for polymers. Cools et al.[144] proposed a graphical extrapolation of the critical composition from the dependence between the elution volume at peak maximum [$E_{pmax}$] and the composition of a binary mobile phase. Cools' method also requires a significant number of measurements similar to the

classical procedure (i.e., SEC-LAC plots) at different compositions of a selected mobile phase with analogous drawbacks. These are avoided by the method proposed by Brun et al.[100,146] and used by Bashir et al.,[145] which requires a single polymer sample of high molar mass and a gradient pump to generate a linear gradient. The critical conditions are then determined as the composition of a mobile phase when the polymer is just desorbed and eluted from the column in the solvent gradient. The value of $E_{pmax}$ for a polymer sample of high molar mass is then used as a basis to refine the critical point for that polymer further using Bashir's method. Bashir's method requires two measurements i.e., one injection of the polymer sample in a solvent gradient and one experiment to determine the composition of the mobile phase in the detector used i.e., the delay volume.

Although polyolefins have been industrially produced for 70 years, conditions for LCCC of polyethylene (PE) or polypropylene (PP) could not be realized until recently, because experimental conditions for their reversible adsorption were not known. The breakthrough came with the application of porous graphitic carbon (PGC) as stationary phase material i.e., when Macko et al. described the separation of PE, PP and ethylene/1-alkene copolymers using porous graphitic carbon (PGC).[7,43] This enabled to realize LCCC for linear polyethylene (PE) by Mekap et al.[53] and of PP by Bhati et al.[54] using the SEC-LAC method as well as the method according to Cools and Bashir. LCCC of *it*-PP and *st*-PP will be identified in this work, using various methods.

### 5.1.1 LCCC of *it*-PP

Four solvents (2-octanol, 2E1H, ODCB and TCB) were chosen as components for the mobile phase. From previous experiments it was known that 2-octanol and 2E1H promote the adsorption of PP onto PGC, whereas ODCB and TCB support its desorption.[9] Using Cools' method conditions for LCCC of *it*-PP in 2-octanol/TCB were determined. The dependencies between the elution volume at peak maximum, $E_{pmax}$, and the concentration of 2-octanol in the mobile phase are shown in Figure 10.

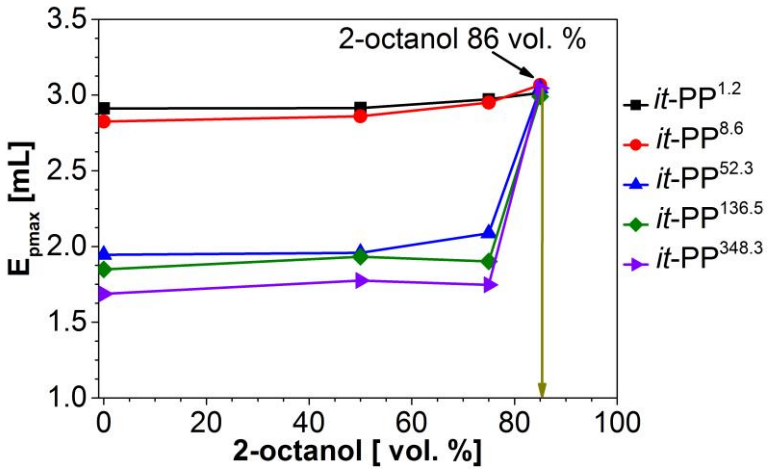



*Figure 10. Relation between $E_{pmax}$ of it-*PP *samples and the composition of the mobile phase 2-octanol/TCB. Temperature: 160 °C. Notice: Composition at crossing of the lines indicates the critical condition (2-octanol/TCB, 86/14 vol. %).*

The solvent composition corresponding to the point of intersection is 86/14 vol. % of 2-octanol/TCB. The determination of critical conditions for *it*-PP according to Bashir's method is illustrated in Figure 11.

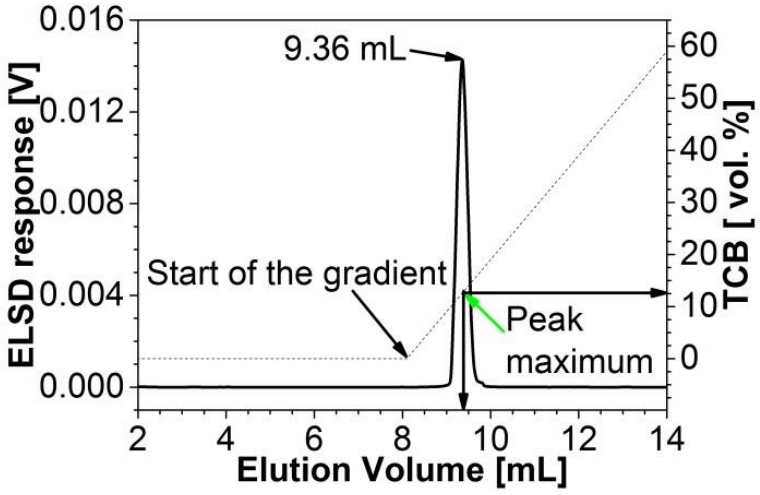



*Figure 11. Chromatogram of it-*PP$^{348.3}$ *in a linear gradient of 2-octanol→TCB. Temperature: 160 °C. Notice: The critical condition (2-octanol/TCB, 87.4/12.6 vol. %) corresponds to the top of the peak.*

LCCC of *it*-PP, identified according to Bashir's method, exists at a solvent composition 87.4/12.6 vol. % of 2-octanol/TCB.

Taking the identified compositions of the mobile phases obtained by these two methods into account, the classical method for determining the critical conditions[55,66,125] was then applied to verify the data. According to this, polymer standards of different average molar mass are injected in a binary eluent, and the chromatographic mode is determined from the elution sequence of the used series of polymer samples: In SEC mode PP with a high average molar mass elutes before PP of low average molar mass, while in LAC the order of elution is inverse. PP elutes at the same volume independent of its molar mass at LCCC. Hence, by controlling the ratio of adsorption/desorption promoting solvent and observing the elution order of PP standards of varying average molar mass, the composition of the mobile phase

required for LCCC can be identified. The chromatograms obtained by the above procedure for the solvent system 2-octanol/TCB are shown in Figure 12.

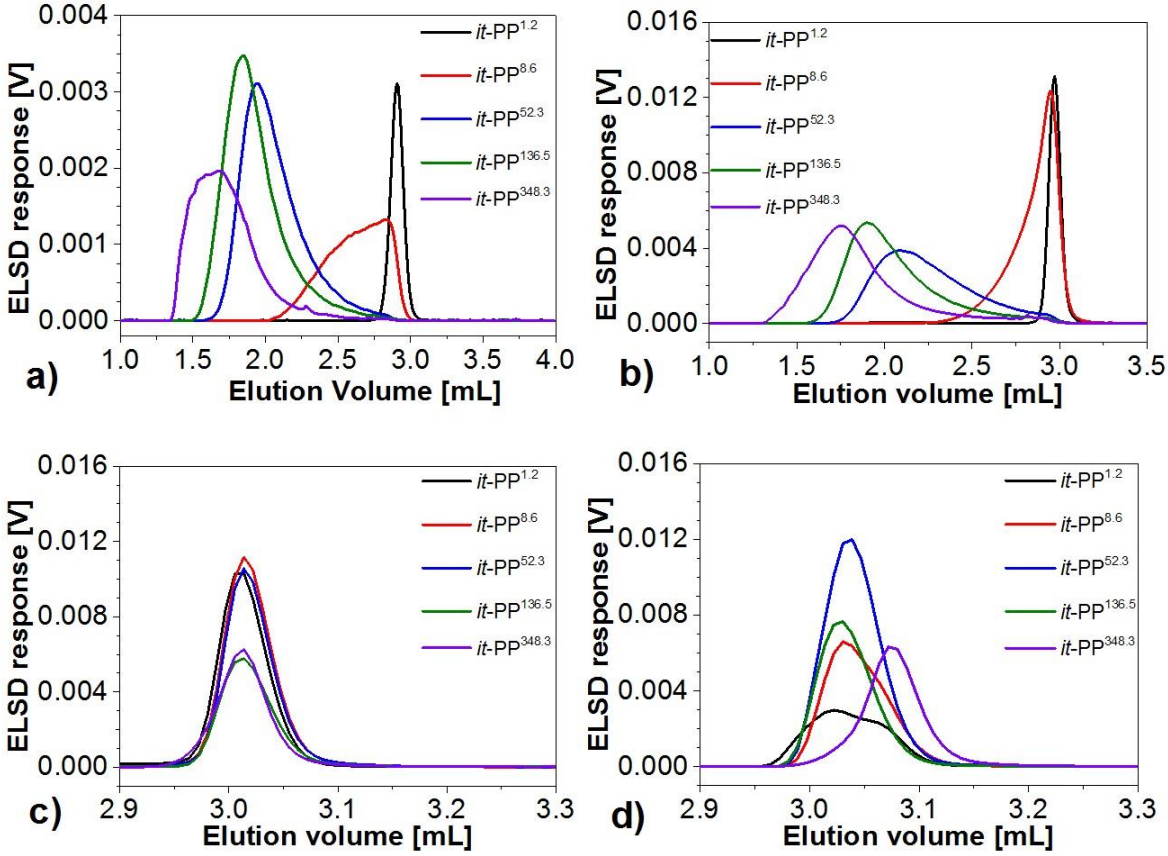



*Figure 12. Overlay of chromatograms of it-*PP *samples. Chromatographic mode and mobile phase: a) SEC: 2-octanol/TCB, 0/100 vol. %, b) SEC to LCCC transition: 2-octanol/TCB, 75/25 vol. %, c) LCCC: 2-octanol/TCB, 87/13 vol. %, d) LAC: 2-octanol/TCB, 92/8 vol. %. Temperature: 160 °C.*

Addition of 2-octanol to TCB increases the retention of *it*-PP and thus shifts the chromatographic mode from SEC to LAC, and a mobile phase composition of 87/13 vol. % of 2-octanol/TCB corresponds to LCCC for *it*-PP (Figure 12). The peak shape changes upon transitioning from SEC → LCCC → LAC and the peaks attain similar shape and width at LCCC (Figure 12). An analogue trend was observed in the other mobile phases (2E1H/TCB, 2-octanol/ODCB and 2E1H/ODCB): The variation in the

peak shape is larger near the critical condition, and the narrowest peak corresponds to LCCC of *it*-PP (Figure 13).

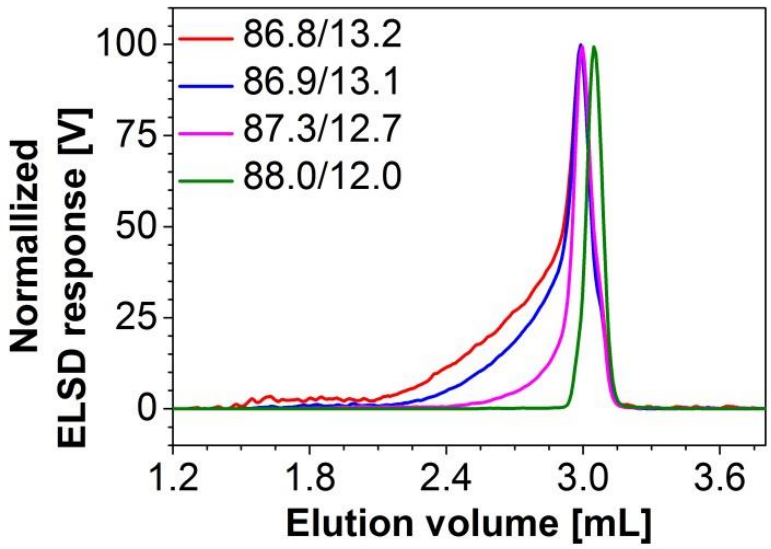



*Figure 13. Overlay of height normalized chromatograms of it-*PP$^{348.3}$*. Mobile phase: 2E1H/TCB. Temperature: 160 °C. Compositions of the mobile phase are indicated in the figure in vol. %.*

Figure 13 shows that small differences in the ratio 2E1H/TCB close to the critical condition for *it*-PP change the shape of the peak which becomes more symmetrical as it approaches to the LCCC mode.

The dependencies between the weight average molar mass, $M_w$, of the *it*-PP samples and $E_{pmax}$ in different mobile phases are presented in Figure 14.

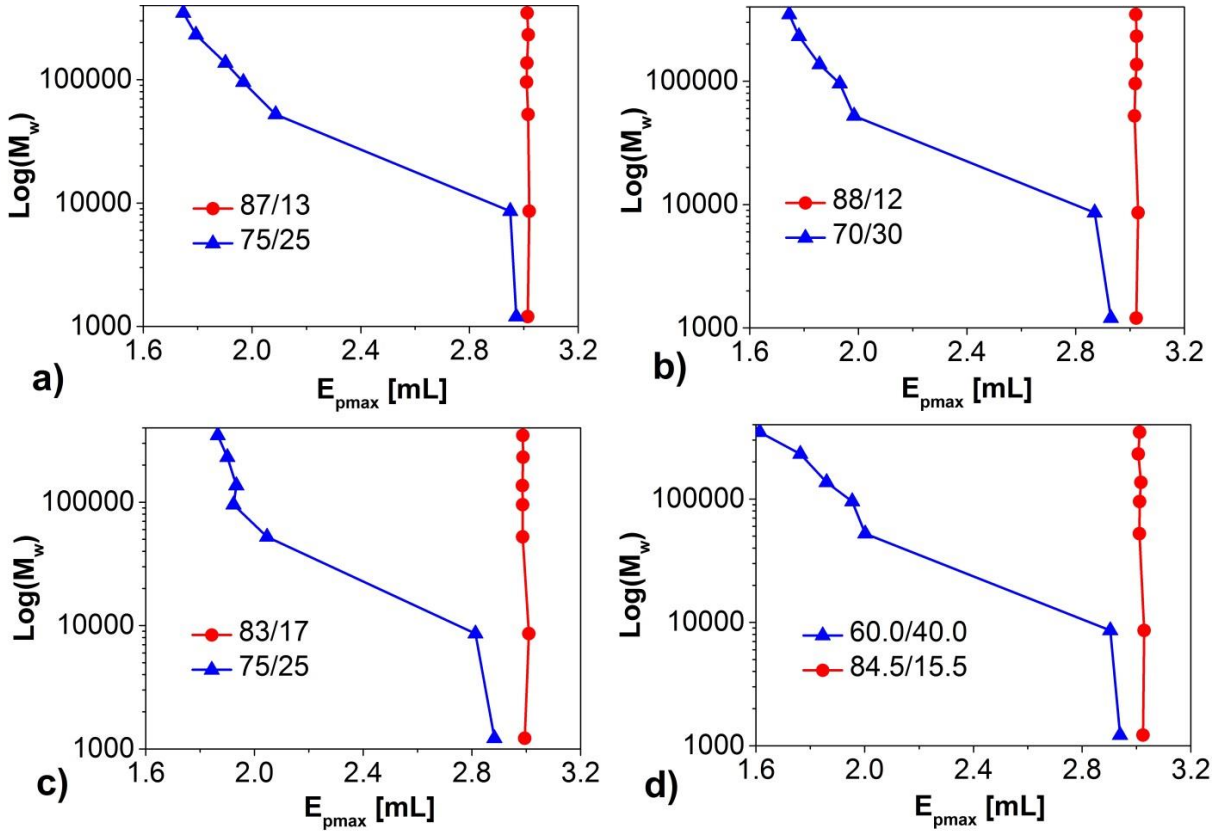



*Figure 14. Relation between $M_w$ of the it-*PP *samples and $E_{pmax}$. Mobile phase: a) 2-octanol/TCB, b) 2E1H/TCB, c) 2-octanol/ODCB and d) 2E1H/ODCB. Temperature: 160 °C. Compositions of the mobile phase are indicated in the figures in vol. %.*

The results in Figure 14a show that an increase in the concentration of the adsorption promoting solvent in the mobile phase increases the elution volumes of the *it*-PP samples. At a specific composition of the mobile phase all samples elute at identical elution volume i.e., irrespective of their molar mass. The compositions of the mobile phase at critical conditions for four different combinations of adsorption and desorption promoting solvents are summarized in Table 6.

*Table 6. Composition of mobile phases corresponding to LCCC for it-PP*

| **Mobile phase** | **SEC-LAC plot [vol. %]** | **Bashir's method [vol. %]** | **Cools' method [vol. %]** |
|---|---|---|---|
| 2-octanol/TCB | 87.0/13.0 | 87.4/12.6 | 86.0/14.0 |
| 2E1H/TCB | 88.0/12.0 | 87.9/12.1 | 86.5/13.5 |
| 2-octanol/ODCB | 83.0/17.0 | 81.0/19.0 | 80.5/19.5 |
| 2E1H/ODCB | 84.5/15.5 | 84.5/15.5 | 83.2/16.8 |

A comparison of the data in Table 6 reveals that the critical conditions for *it*-PP determined in different mobile phase systems with the classical method are in good agreement with the values obtained by Bashir's and Cools' methods. Furthermore, it can be recognized that the concentration of TCB required for desorption of *it*-PP is lower compared to that of ODCB in the mobile phase composition at LCCC of *it*-PP, which is in line with observations made by Mekap et al.[53] With regard to the adsorption promoting strength 2-octanol is a slightly weaker eluent compared to 2E1H.

### 5.1.2 LCCC of *st*-PP

Previous LAC experiments have revealed that *st*-PP is stronger adsorbed on a PGC surface than the other stereochemical variants, with the order of elution and therefore the extent of interaction with the graphite surface being *it*-PP<*at*-PP<*st*-PP.[7,9] Hence, it can be expected that it will require a larger concentration of a desorption promoting solvent in the mobile phase to reach critical conditions for *st*-PP compared

to *it*-PP or *at*-PP. Analogous to *it*-PP, the critical conditions for *st*-PP were identified in 2E1H/ODCB (Figure 15).

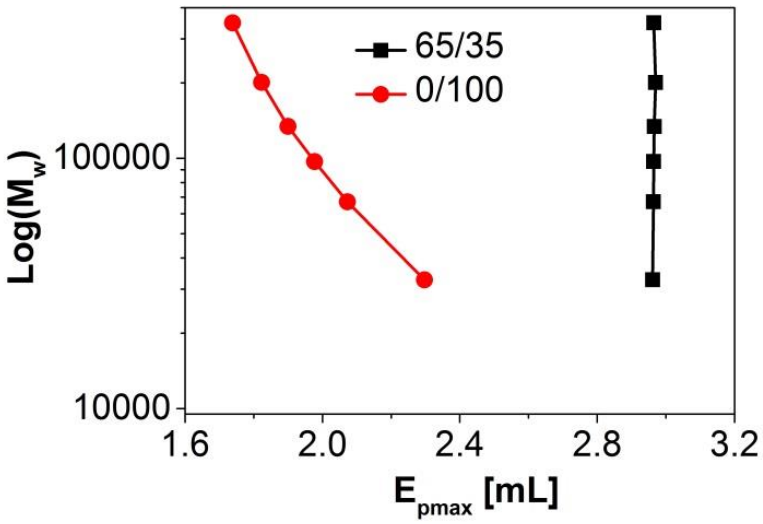



*Figure 15. Relation between $M_w$ of the st-PP samples and $E_{pmax}$. Mobile phase: 2E1H/ODCB, composition is indicated in the figure in vol. %. Temperature: 160 °C.*

Figure 15 shows that *st*-PP samples with different weight average molar masses coelute at 65/35 vol. % of 2E1H/ODCB. On the other hand, the realization of LCCC of *it*-PP required only 15.5 vol. % of ODCB in the mobile phase 2E1H/ODCB (Figure 14d). This confirms that the adsorptive interactions of *st*-PP with PGC are more intensive compared to those of *it*-PP.

### 5.1.3 Influence of temperature on LCCC of *it*-PP

In general, *it*-PP is only soluble at elevated temperature. To probe the influence of temperature, the critical conditions for *it*-PP in 2E1H/TCB and 2E1H/ODCB were identified using Bashir's method in the range 140 – 180 °C. A variation in temperature will require an adjustment in the mobile phase composition to maintain the critical conditions[55] and the attain Gibbs free energy (ΔG) a value of zero again at the new

temperature. The relationship between the percentages of desorption promoting solvent in the mobile phase at critical conditions and the temperature is illustrated in Figure 16.

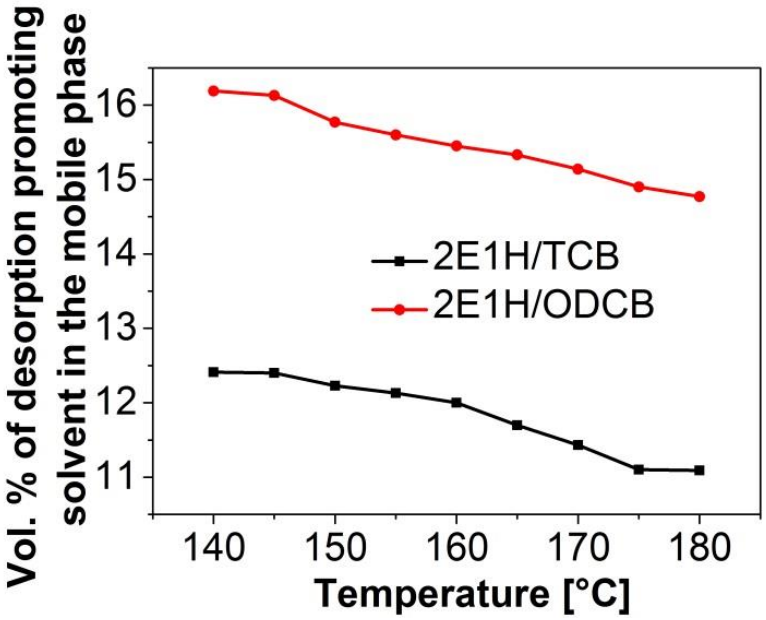



*Figure 16. Relation between the fraction of desorption promoting solvent in the mobile phase and the temperature at the LCCC of it-PP. Mobile phases are shown in figure.*

As the interactions between the PGC surface and PP decrease when the temperature is raised, the amount of desorption promoting solvent in the mobile phase required to reach LCCC of *it*-PP decreases. The dependency between the fractions of desorption promoting solvent and temperature is almost linear. The same trend is observed when TCB is used as thermodynamically good solvent. Figure 16 also reveals that the amount of TCB required for desorption of *it*-PP is lower compared to that of ODCB.

### 5.1.4 Separation of PP on the basis of tacticity at critical conditions

One of the applications of LCCC would be to selectively separate PP on the basis of tacticity. Samples of *it*-PP, *at*-PP and *st*-PP with high average molar mass were injected

into the Hypercarb™ column flushed with 2E1H/ODCB (65/35 vol. %) at 160 °C i.e., at critical conditions for *st*-PP.

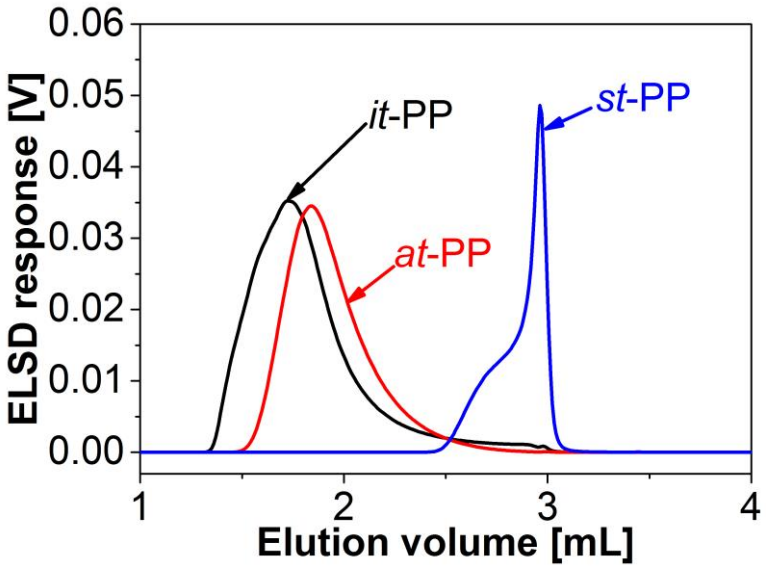



*Figure 17. Overlay of chromatograms of it-PP$^{348.3}$, at-PP$^{315}$ and st-PP$^{196.8}$ at critical conditions for st-PP. Mobile phase: 2E1H/ODCB, 65/35 vol. %. Temperature: 160 °C.*

The results in Figure 17 illustrate that PP can be separated according to tacticity at critical conditions for *st*-PP. The advantage of using LCCC of *st*-PP is that *st*-PP can be separated from *it*-PP and *at*-PP in an isocratic solvent flow. To evaluate how the separation is influenced by the molar mass of the atactic and isotactic variant, samples of *it*-PP and *at*-PP with different weight average molar masses were injected into the Hypercarb™ column at LCCC of *st*-PP.

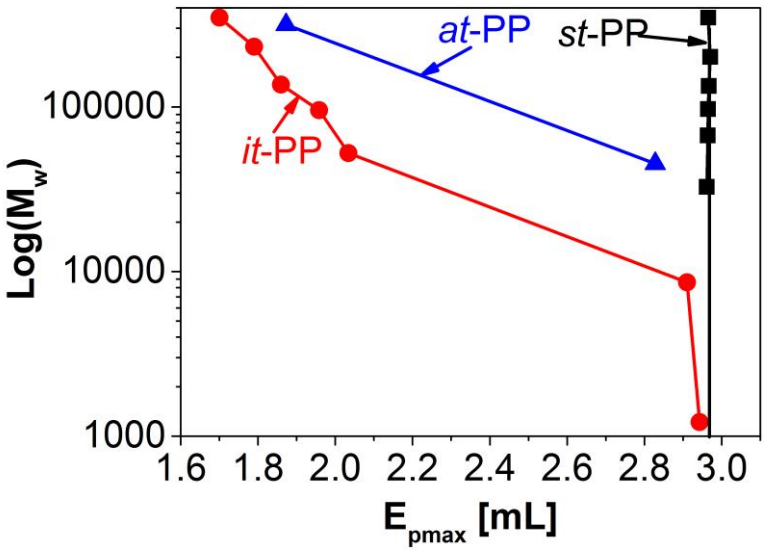



*Figure 18. Relation between the weight average molar mass ($M_w$) and $E_{pmax}$ of both it-PP and at-PP samples at critical conditions for st-PP. Mobile phase: 2E1H/ODCB, 65/35 vol. %. Temperature: 160 °C.*

Figure 18 demonstrates that this chromatographic system enables to separate *st*-PP (different $M_w$ eluting at same elution volume at LCCC) from *at*-PP and *it*-PP over their full range of $M_w$. An isocratic separation of PP according to tacticity and weight average molar mass was never before described in the literature. One of the applications of LCCC would be to overcome the molar mass influence in the separation according to microstructure or composition, which is inherently present when using SGIC.[7]

### 5.1.5 Separation of PP-HI at critical conditions of *it*-PP

PP-HI is an important industrially produced material with versatile properties, which consists of a semi-crystalline component (e.g., *it*-PP) and a rubbery phase (e.g., EP copolymers). When analyzing a PP-HI sample at LCCC of *it*-PP it was found that the EP part was adsorbed on the stationary phase, which could then be eluted by

switching the mobile phase to the pure thermodynamically good solvent. The separation of two PP-HI samples with different average ethylene content in the EP copolymers using this approach is illustrated in Figure 19.

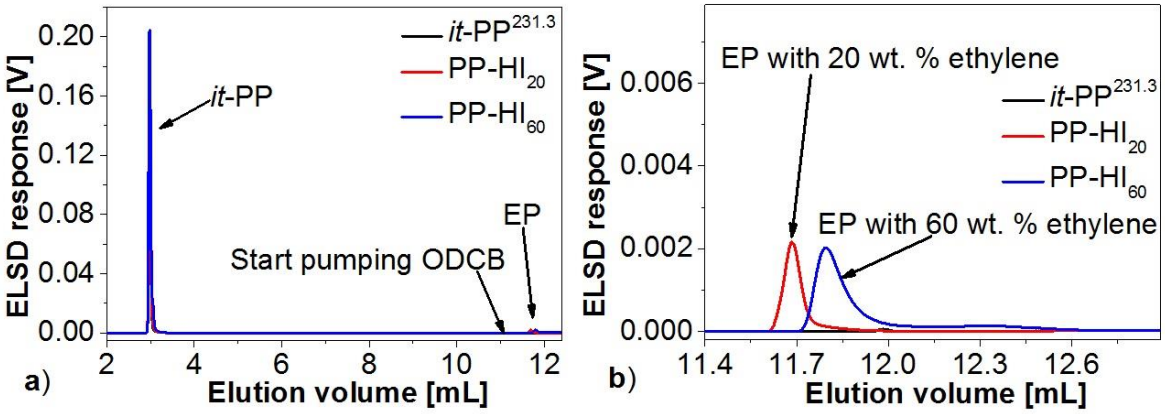



*Figure 19. Overlay of chromatograms corresponding to two PP-HI samples: a) Large peaks corresponding to it-PP and very small peaks corresponding to the EP copolymers, b) The EP peaks after zooming. Mobile phase: 2-octanol/ODCB (83/17 vol. % before pumping 100 vol. % ODCB). Temperature: 160 °C.*

*it*-PP eluted in the LCCC mode at the critical conditions for *it*-PP. On the contrary, the EP copolymers, which are a constituent of the PP-HI, were adsorbed on the PGC surface and eluted only after pumping pure ODCB (Figure 19). As can be expected from the strong adsorption of ethylene sequences with the PGC surface the EP copolymer with larger average ethylene content was stronger adsorbed and therefore eluted later. Thus, by using a sequence of LCCC followed by pure desorption promoting solvent both constituents of PP-HI could be baseline separated and detected. In difference to the previously described HT-LAC systems for the separation of PP-HI, which required gradient elution (1-decanol→TCB[40,147] or n-

decane→TCB[148]), the HT-LAC system described here uses two eluents (2-octanol/ODCB and ODCB) at constant composition.

Considering the elugrams in Figure 19 and taking into account that the fraction of EP copolymer present in the PP-HI as determined from CRYSTAF is 24.9 % in PP-$HI_{20}$ and 24.6 % in PP-$HI_{60}$, the peak of the EP copolymer part is of very low intensity and does not reflect the portion of EP copolymer present in the PP-HI. This is due to the fact that the ELSD is a semi-quantitative detector and its signal is in a complex manner influenced by the nature of the mobile phase and the molecular parameters of the polymer.[140] Hyphenating LAC with SEC (HT 2D-LC) leads to a quasi-isocratic elution in the second dimension. This in turn enables to use infrared spectroscopy for detection[141], as the thermodynamically good solvents of the second dimension are IR transparent in the aliphatic wavelength region.

A model High Impact PP sample (M-PP-HI), containing $EP_{60}$ and *it*-$PP^{136.5}$ in a 1/1 ratio, was analyzed by HT 2D-LC. The *it*-PP part, which is present in the sample, will elute independent of its molar mass at conditions for LCCC of *it*-PP, and eluting the EP copolymer will require to either apply a solvent gradient (Table 2) or to pump pure desorption promoting solvent. The cumulated SEC traces of the HT 2D-LC analysis of M-PP-HI are illustrated in Figure 20. Both the ELSD and the IR responses are presented in Figure 20.

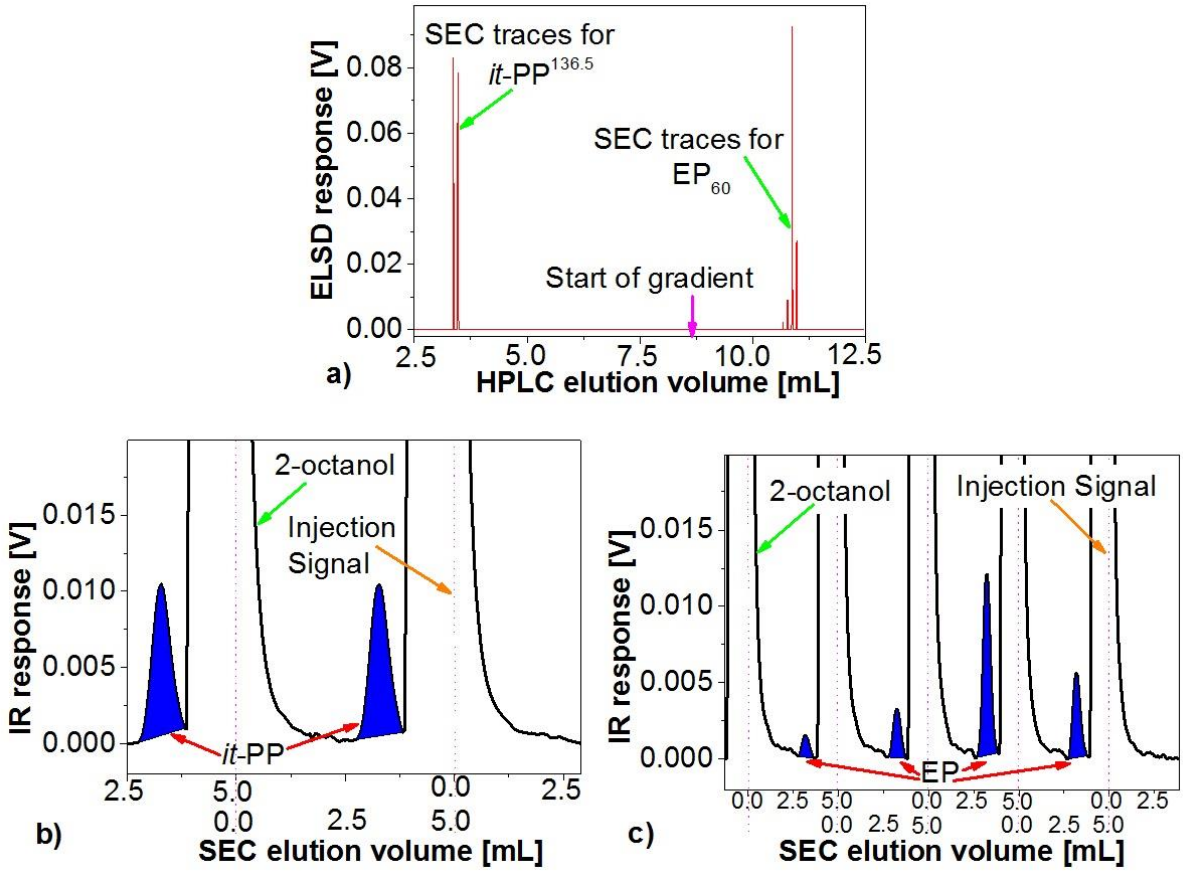



*Figure 20. SEC traces of the HT 2D-LC analysis of M-PP-HI: a) ELSD response, b) IR response for it-PP (Total carbon –CH), c) IR response for EP copolymer (Total carbon –CH). Mobile phase: 2-octanol/TCB, 87/13 vol. %. Gradient program according to Table 3 (short gradient). Temperature: 160 °C.*

The cumulated areas under the curves (Figure 20b, c) for EP and *it*-PP were compared, and they were found to be similar (ratio 1.05/1), which reflects their fractions in the blend. The color coded contour plot of the HT 2D-LC-IR separation of M-PP-HI, which was generated from the SEC traces, is shown in Figure 21.

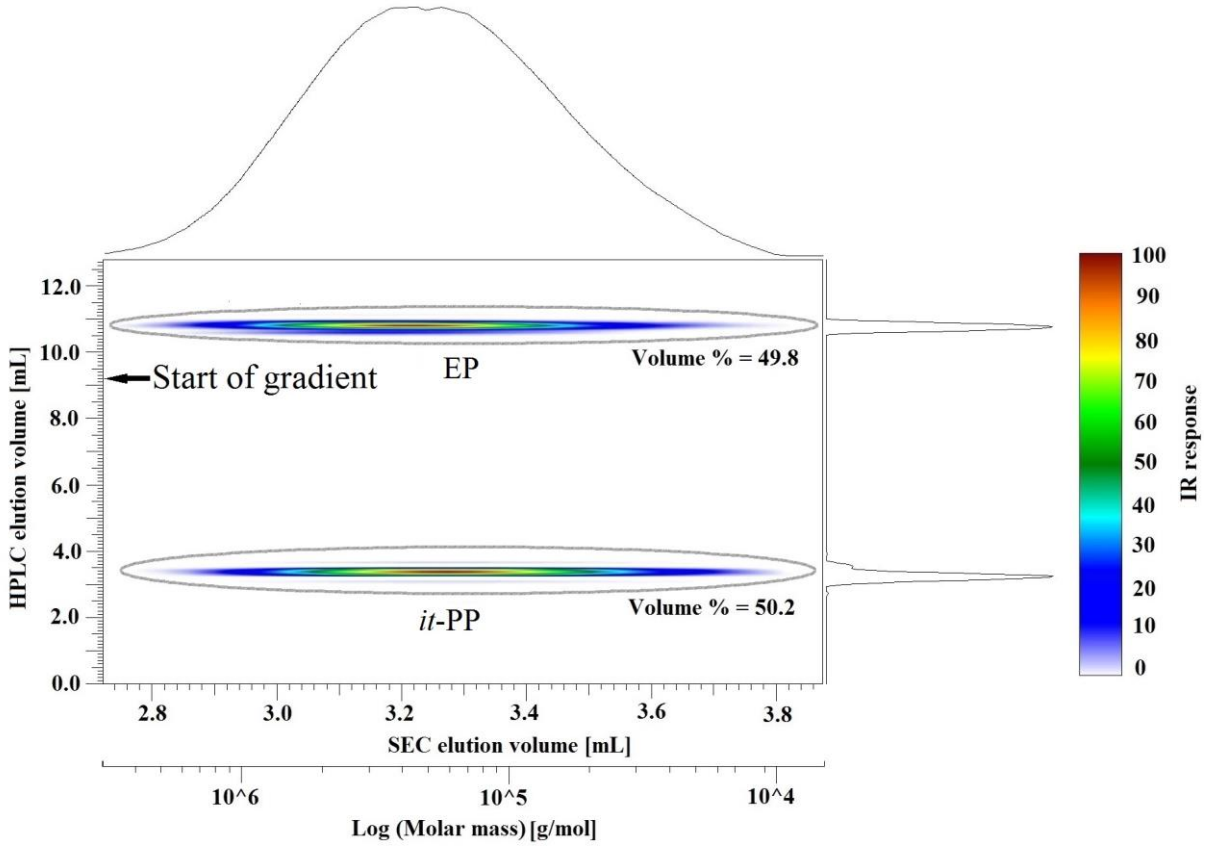



*Figure 21. Contour plot illustrating the HT 2D-LC separation of M-PP-HI (it-PP$^{136.5}$ + EP$_{60}$) recorded with the IR4 detector. Mobile phase: 2-octanol/TCB, 87/13 vol. %. Temperature: 160 °C.*

The contour plot illustrates a base-line separation of both basic constituents on the LAC axis, and it also delivers the molar mass distribution (X-axis – calibration with PE standards) for the components of the blend. The average molar masses are shown in Figure 21 together with the SEC elution volume, which can be converted according to universal PS calibration using appropriate Mark-Houwink constants. Individual spots in the contour plot can be used to determine the quantity of a component that is eluting in that spot. The ratio of the quantities of *it*-PP and EP was obtained from the contour plot as 1.01/1, which reflects the fractions of individual components in the model blend.

## 5.2 New method to determine the LCCC

Berek et al. pointed out the problem of limited recovery of the sample from the column, connected with LCCC in some polymer/solvent/sorbent systems. The sample recovery from the column rapidly decreases with increasing weight average molar mass and approaches zero for macromolecules between 100,000 and 500,000 g/mol.[56,149-151] The dependence of sample recovery on its molar mass also means that the high molar mass fractions of a broadly distributed polymer sample might be selectively retained within the column, which then may lead to an error in the determination of the critical point. Consequently, the determined molar mass distributions and derived molar masses of polymers obtained from 2D-LC by coupling LCCC with SEC (LCCC x SEC) will be erroneous also for that part of macromolecules which is otherwise separated in the SEC mode.[56,151] Commercially available polyolefins regularly contain high or even ultra-high molar mass fractions, which may eventually be adsorbed at critical conditions. Therefore, a new method for determination the critical point will be described, which is based on monitoring the recovery of a single polymer sample with high average molar mass from a column. The new method will be applied to identify conditions for LCCC of *it*-PP, *st*-PP and PE.

### 5.2.1 Determination of the critical conditions for *it*-PP using the new method

*it*-PP$^{348}$ was dissolved in an adsorption promoting solvent (2-octanol) and then the solution was injected into the column flushed with a binary mobile phase (2-octanol/ODCB) at a particular composition (with a higher percentage of adsorption promoting solvent). In the subsequent injection the composition of the mobile phase was changed accordingly to reduce the adsorption of the polymer in the Hypercarb$^{TM}$

column. This process was repeated until no fraction of the polymer was adsorbed on the stationary phase. The elugrams for selected injections are shown in Figure 22.

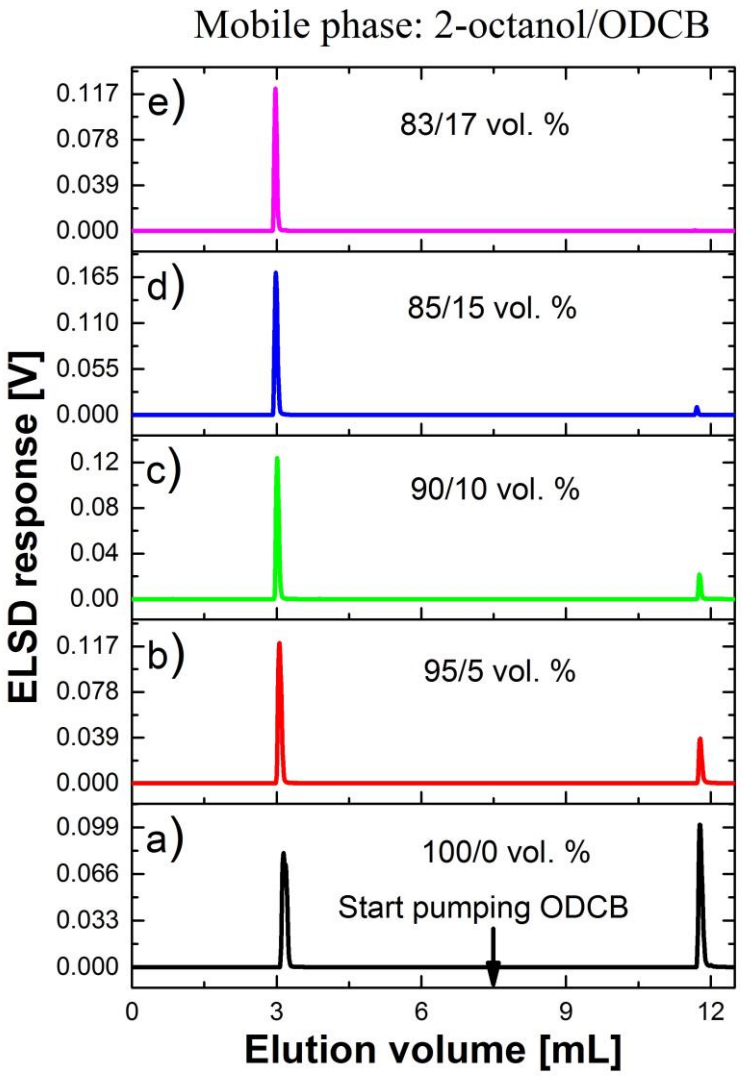



*Figure 22. Stack plot with elugrams in different mobile phase compositions for it-PP*[348].

A part of *it*-PP[348] sample eluted from the column (Figure 22a), while another portion of the sample was adsorbed in the column. The latter was then desorbed by purging pure ODCB into the column – leading to the appearance of the second peak of *it*-PP[348] in the chromatogram (Figure 22a). The composition of the binary mobile phase was then changed, *it*-PP[348] was again injected and the adsorbed part of the sample was

eluted after pumping pure ODCB. From Figure 22b, d it can be inferred that the increase in the concentration of the desorption promoting solvent leads to a rising intensity of the first peak, while the peak eluting after pumping pure ODCB decreases in intensity. Finally, at the critical conditions (i.e., 83/17 vol. % of 2-octanol/ODCB), the sample is eluted in a single peak (Figure 22e). *it*-PP[348] will elute in SEC mode at higher concentration of the desorption promoting solvent i.e., the first composition of the mobile phase at which the polymer is fully eluted corresponds to the critical conditions (Figure 22e).

### 5.2.2 Determination of the critical conditions for *st*-PP using new method

In general, *st*-PP is stronger adsorbed on the porous graphitic carbon surface compared to *it*-PP and, thus, it requires a larger concentration of the desorption promoting solvent (TCB or ODCB) to desorb the adsorbed *st*-PP from the graphitic surface.[152] The stack plot shown in Figure 23 illustrates the identification of critical conditions for *st*-PP in the mobile phase 2-octanol/ODCB using the new method.

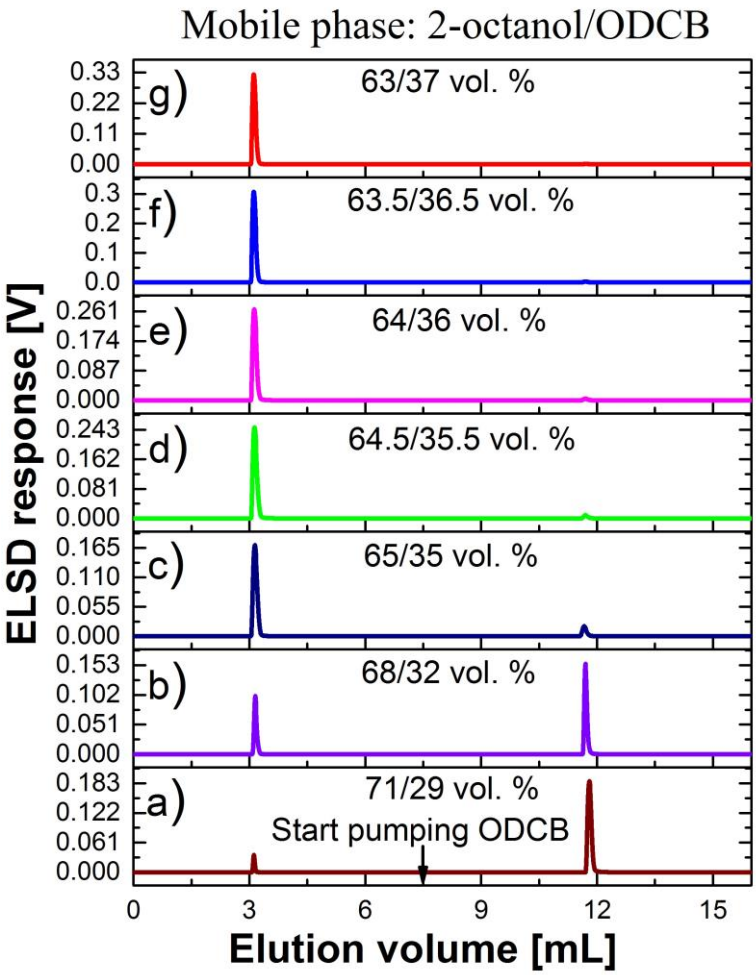



*Figure 23. Stack plot with elugrams in different mobile phase compositions for st-PP*[196].

The composition for LCCC for *st*-PP is identified as 63/37 vol. % of 2-octanol/ODCB (Figure 23g).

### 5.2.3 Determination of the critical conditions for PE using new method

The solvent composition at which PE[181] fully eluted as a single peak and no portion of it eluted after pumping pure ODCB into the column corresponds to the critical conditions for PE in the mobile phase 2-octanol/ODCB at 160 °C. An overlay of the chromatograms for PE[181] at different ratios of 2-octanol/ODCB is shown in Figure 24.

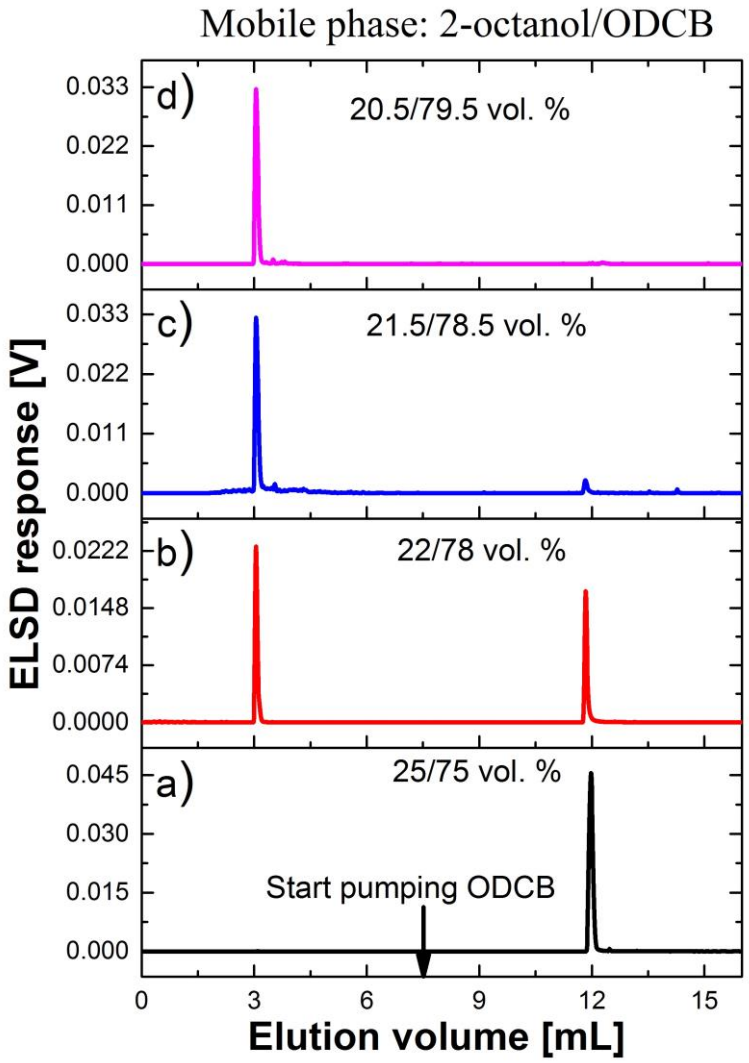



*Figure 24. Stack plot with elugrams in different mobile phase compositions for PE*[181].

The condition for LCCC for PE is identified as 20.5/79.5 vol. % of 2-octanol/ODCB (Figure 24d).

The critical conditions for *it*-PP, *st*-PP and PE were determined in different solvent pairs[53,54] using the three methods described in the introduction and the results were compared with those obtained using the new method in Table 7.

*Table 7. Composition of mobile phases under critical conditions for it-PP, st-PP or PE. Column: Hypercarb™. Temperature: 160 °C.*

| **Polymer and mobile phase** | **SEC-LAC method [vol. %]** | **Bashir's method [vol. %]** | **Cools' method [vol. %]** | **New method [vol. %]** |
|---|---|---|---|---|
| *it*-PP 2-octanol/ODCB | 83/17 | 81/19 | 80.5/19.5 | 83/17 |
| *st*-PP 2-octanol/ODCB | 65/35 | 64.2/35.8 | 63.5/36.5 | 63/37 |
| PE 2-octanol/ODCB | 21/79 | 21.5/78.5 | _ | 20.5/79.5 |
| *it*-PP 2E1H/TCB | 88/12 | 87.9/12.1 | 86.5/13.5 | 88/12 |
| *st*-PP 2E1H/ODCB | 65/35 | 66.8/33.2 | _ | 64/36 |
| PE n-decane/TCB | 51.5/48.5 | 50.8/49.2 | 52/48 | 52/48 |

The critical compositions of the mobile phase for *it*-PP in 2-octanol/ODCB as well as in 2E1H/TCB obtained with the new method are identical with the critical compositions determined using the SEC-LAC plot method. The same is valid for critical composition of the mobile phase for PE in n-decane/TCB obtained with the new method and Cools' method. Good agreement in the critical composition of the

mobile phase for *st*-PP in 2-octanol/ODCB is found between the results obtained with the new method and Cools' method.

Deviations in the critical compositions of the mobile phases are observed between Bashir's method and the new method (Table 7) for all cases. This can be explained by the fact that the value of the critical composition is determined from $E_{pmax}$ of a single polymer peak when using Bashir's method. For this purpose it is usually expected that the shape of the solvent gradient in a detector is proportionate to the shape of the gradient in the pump, being delayed by the volume (time) the gradient requires to reach the detector. It is known that the shape of the solvent gradient in the detector not always correlates with the shape of the gradient generated in the pump, due to the effects of pore diffusion as well as the differing viscosity of constituents of the gradient.[153] As a result, the supposed critical composition of the mobile phase corresponding to the top of the polymer peak may vary from that of real LCCC. The SEC-LAC plot method as well as Cools' method use elution volumes of series of polymer standards measured at isocratic conditions and thus yield more authentic values of the critical compositions of mobile phases (Table 7) compared to Bashir's method (only one polymer sample used in a solvent gradient). The new method also utilizes isocratic mobile phases.

We summarize that a solvent gradient (as required with Bashir's method), a series of polymer samples (as required with the SEC-LAC plot method and Cools' method), defined shape of peaks (symmetrical or asymmetrical) or precise values of elution volumes (as required with all three methods) are not a prerequisite of the new method, which apparently has a positive effect on the authenticity of the obtained results. Moreover, the recovery of the polymer samples of interest in LCCC is

controlled, an aspect of particular importance for commercial olefin copolymers, which regularly contain high molar mass fractions.

## 5.3 Quantification of identical and unique segments in EP

Different copolymer samples of EP contain some amount of unique segments (i.e., have different molar mass and chemical composition) and a certain amount of identical segments (having similar coordinates with regard to molar mass and chemical composition). In this work EP copolymers with different average chemical composition will be analyzed using HT 2D-LC/IR and a method for quantifying the identical and unique segments in the samples will be described. The contour plots corresponding to these EP copolymers will be created and the matrices (termed as "Matrix approach") corresponding to those contour plots will be used for the quantification.

### 5.3.1 Comparison of ELS detector and IR-detector response from HT 2D-LC

PE[116] was dissolved in 1-decanol and injected into the Hypercarb™ column using the solvent gradient program shown in Table 2. A comparison between the response of the ELS detector and that of the IR4-detector is shown in Figure 25.

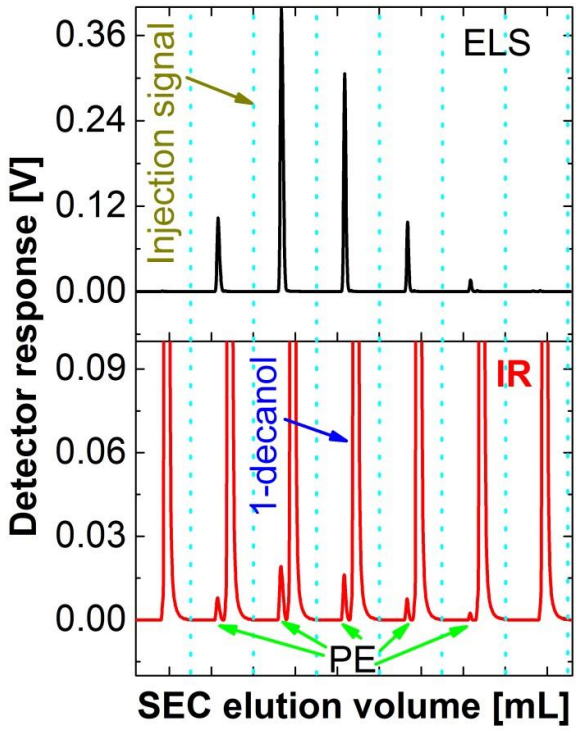



*Figure 25. Comparison of the response of PE$^{116}$ obtained with the IR4-detector ($IR_1$ signal) and ELS detector. HT 2D-LC method No. 4 was used (Table 3). The broken line indicates injection of a sample solution (7.5 mL volume between 2 SEC injections).*

The same number of peaks corresponding to PE is obtained with both detectors, yet it can be observed that the IR response for the polymer is significantly lower compared to that of the solvent (1-decanol).

Height and area ratios of the ELSD response to the IR response for the peaks of PE as obtained from HT 2D-LC analysis (Figure 25) are shown in Figure 26.

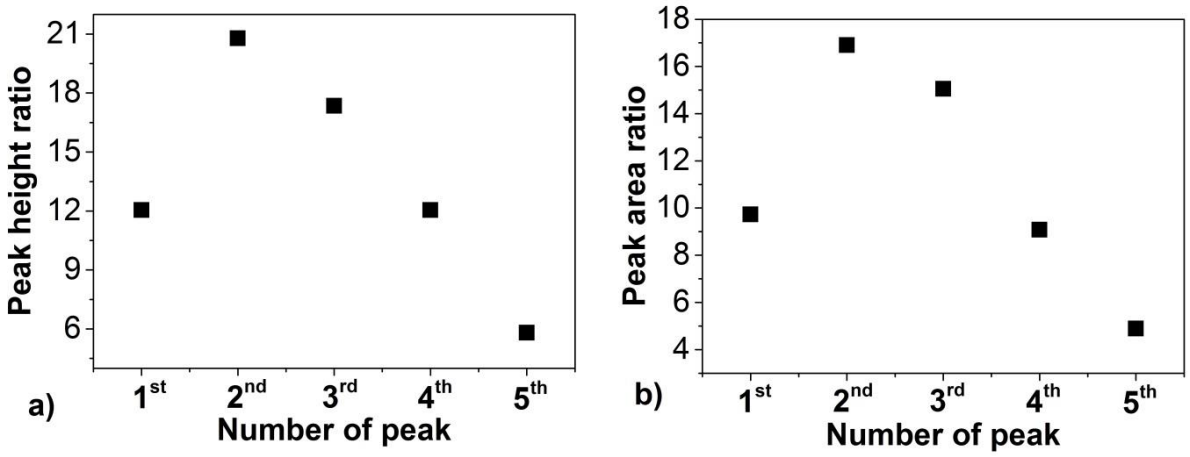



*Figure 26. Ratio ELSD response/ IR-detector response for PE[116] ($IR_1$ signal): a) Peak height ratio and b) Peak area ratio. 2D-LC method No. 6 was used (Table 3).*

The ratio of heights and areas varied to a large extent, when the response of IR and that of the ELSD are compared (Figure 26). These variations are caused by the non-linear response of the ELSD. While the response of the IR-detector increases linearly with the concentration of an analyte, the response of an ELSD increases exponentially. As a result the ELSD overestimates especially the higher concentrations.

### 5.3.2 Optimization of the solvent flow rate in the first dimension of HT 2D-LC

While the solvent is "invisible" due to evaporation when using an ELS detector, interference of the solvent peak with the polymer peak may become an obstacle when using IR-detection in HT 2D-LC. This solvent peak could be eliminated from the chromatograms if an IR transparent solvent for the tuned wavelength region would be found, which at the same time supports the adsorption of the analyte. The other option is to improve the separation between the peak of the solvent and that of the polymer. Therefore, the LAC flow rate has to be optimized with the aim to separate

the solvent and the polymer peak from each other. SEC-traces (where polymer is eluting) obtained from HT 2D-LC analyses of $PE^{116}$ are shown in Figure 27.

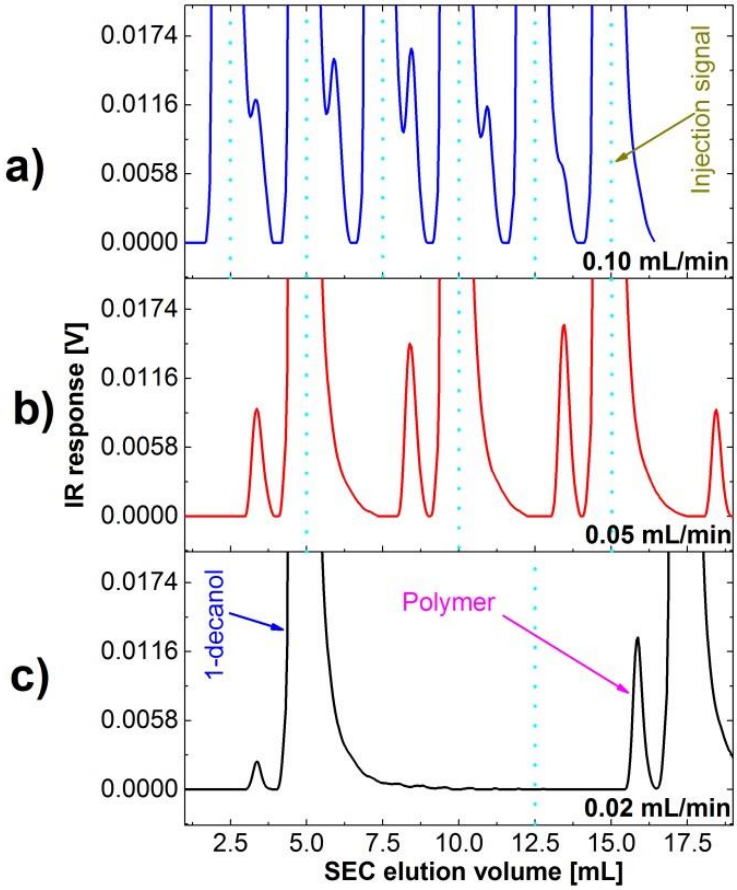



*Figure 27. SEC-traces of $PE^{116}$ recorded with IR4 detector ($IR_1$ signal) at the following flow rate in LAC column: a) 0.10 mL/min (2D-LC Method 1 described in Table 3 was used), b) 0.05 mL/min (Method 2) and c) 0.02 mL/min (Method 3). The dotted lines in the figures indicate the injection signals.*

The peaks of PE were overlapping with the peak of 1-decanol from the previous injection at an LAC flow rate of 0.10 mL/min (Figure 27a). On the contrary, the peaks corresponding to 1-decanol and the polymer were well separated from each other when the LAC flow rate was reduced to 0.05 mL/min (Figure 27b), as this increases the time interval between two injections into the SEC column. Lowering the flow rate

in the LAC column further to 0.02 mL/min (Figure 27c) resulted in a better separation of the PE fractions from the solvent peak. Reducing the SEC flow rate increased the separation between the polymer and the solvent peak. The size of the separation window in SEC is shown in Figure 28 for different combinations of flow rates in LAC and SEC.

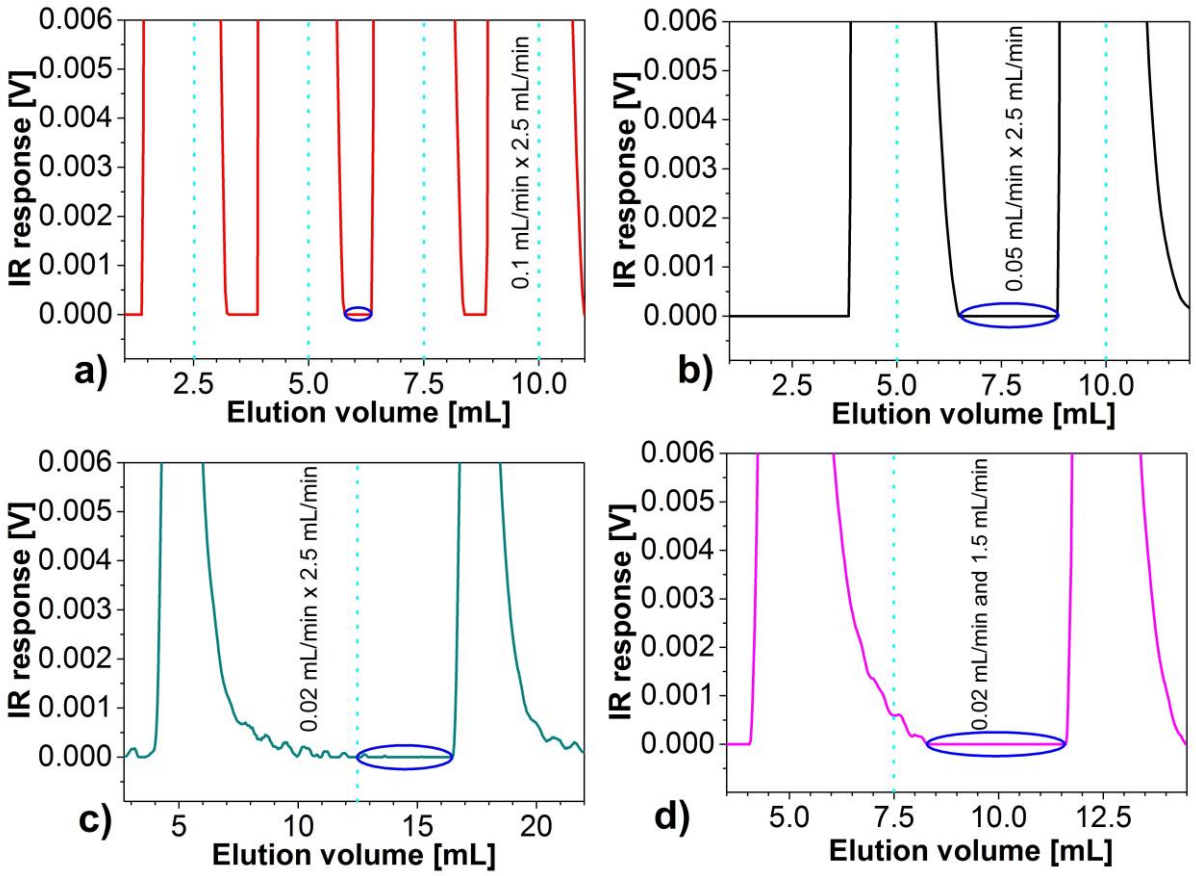



*Figure 28. Separation window for a polymer peak: a) 2D-LC method No. 1 (Table 3), b) method No. 2 and c) method No. 3, d) method No. 4. Flow rates LAC x SEC are stated in the figure. The dotted lines in the figures indicate the injection signals and the blue circles indicate the separation window available for a polymer sample.*

The size of the separation window at different solvent flow rate combinations (LAC x SEC) is presented in Table 8.

*Table 8. Separation window at different flow rates in LAC and SEC.*

| LAC flow rate [mL/min] | SEC flow rate [mL/min] | Separation window [mL] |
|---|---|---|
| 0.1 | 2.5 | 0.5 |
| 0.05 | 2.5 | 2.27 |
| 0.02 | 2.5 | 3.93 |
| 0.02 | 1.5 | 3.27 |

The largest separation window is observed at an LAC flow rate of 0.02 mL/min (Figure 28c). The LAC flow rate of 0.05 mL/min is chosen as optimum flow rate as it provides a sufficient separation window for the EP copolymers to elute and at the same time requires less time for a full HT 2D-LC analysis (Figure 28b).

### 5.3.3 Representation of the quantitative data as a contour plot

$EP_{59.7}$ was analyzed with HT 2D-LC and the SEC-traces are shown in Figure 29a, b. The solvent peaks were excluded and only the SEC-traces corresponding to the polymer were selected (Figure 29c) to generate a color coded contour plot (Figure 29d).

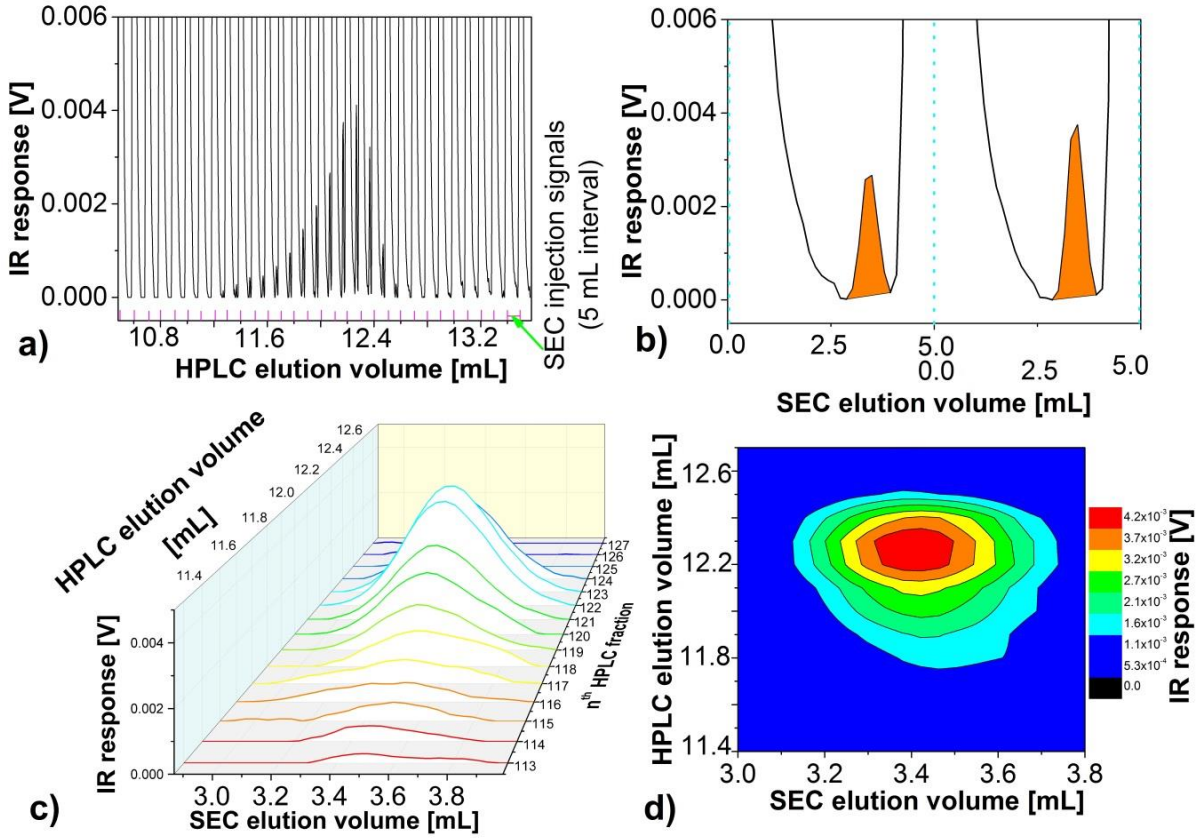



*Figure 29. SEC-traces for sample $EP_{59.7}$: a) Response of the IR4 ($IR_1$ signal), b) zoomed at the central peaks, c) stacked SEC-traces (fraction 113 – 127), d) color coded contour plot. Concentration: 1 mg/mL. 2D-LC method No. 2 was used (Table 3).*

The sample eluted in 15 fractions (fraction 113 – 127) from the LAC column i.e., 15 SEC analyses were used to generate of the contour plot (Figure 29d). This contour plot can be represented as a matrix with *i* number of rows (number of rows equals to number of points or the IR responses from one SEC analysis) and with *j* number of columns (number of columns equals to number of the LAC fractions) i.e., with *i* x *j* number of elements ($E_{i,j}$). The mass of polymer, the average molar mass and the average ethylene content corresponding to each element $E_{i,j}$ as well as to each LAC fraction can be calculated by applying corresponding calibrations (concentration of

polymer vs. response of the IR detector, average molar mass vs. SEC elution volume and average chemical composition vs. LAC elution volume).

### 5.3.4 Calibrations

Ortin et al. demonstrated that the response of the IR4 detector ($IR_1$ signal) is independent of the CC of EP copolymers.[143] The mass of polymer in each element of the matrix can be calculated from a calibration curve, which expresses the dependence between the mass of polymer and the response of the IR detector (Total carbon –CH). Such a calibration curve can be obtained by injecting solutions with varying concentration of the polymer and plotting the IR response with respect to the injected concentration. An alternative way is to inject a polymer solution with known concentration and partition the SEC elugram into identical slices (e.g., 100 $\mu$L). Then, the average IR response of the individual slice can be plotted against the mass of polymer eluting in that slice, which can be derived from the total injected mass of polymer. This method can be applied for both symmetrical and asymmetrical peaks. Another advantage of this approach is that only a single injection is required for this calibration, hence the sources of error, which inevitably happen while using stock solutions, are reduced.

A solution of sample $EP_{59.7}$ in TCB was injected into the SEC column and the elugram of the sample is shown in Figure 30.

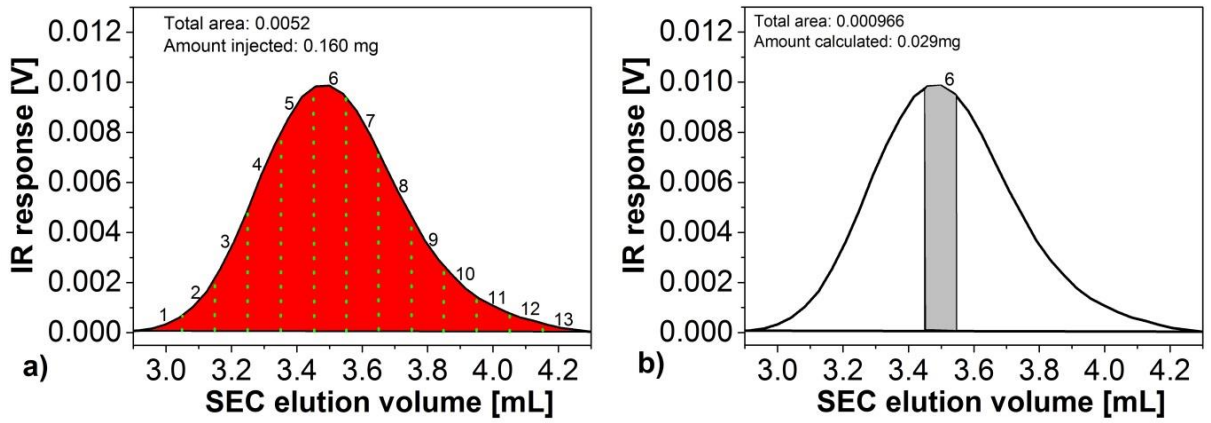



*Figure 30. SEC chromatogram for sample $EP_{59.7}$: a) Area of the peak, b) Area corresponding to 100 μL in 6th fraction of the chromatogram. Solvent flow rate in SEC: 2.5 mL/min, injection loop: 100 μL.*

The total area of the polymer peak (Figure 30a) corresponds to the mass of the polymer injected into the SEC column and eluted over a volume of 1400 μL. This elugram was divided into 100 μL slices (the volume of the injection loop), and the area corresponding to each volume fraction was calculated and put into relationship with the total area of the elugram to obtain the mass of polymer eluting in each fraction (Figure 30b). Using this method a relation between the IR response and the mass of polymer eluted was obtained (Figure 31).

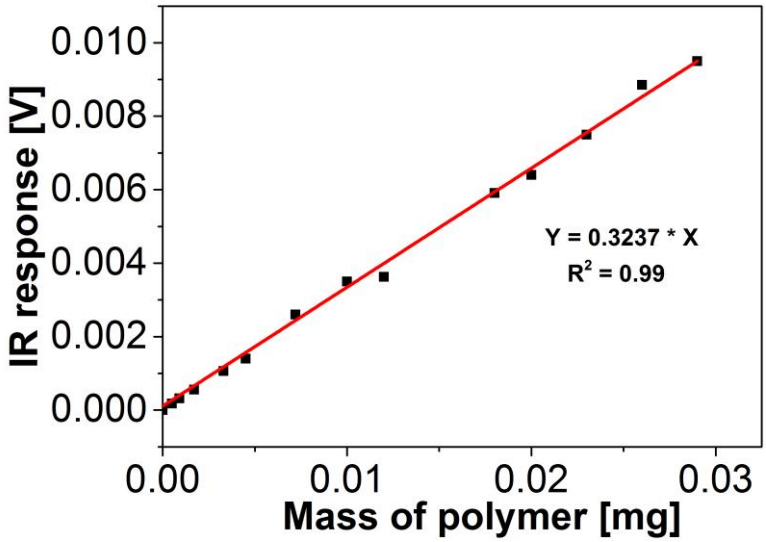



*Figure 31. Relation between the IR response (peak height) and the mass of sample $EP_{59.7}$ copolymer.*

A linear relationship between the IR response and the mass of the EP copolymer (Figure 31) is expressed in Equation 13. The reproducibility of the results was checked by injecting the sample three times and the standard deviation observed in the IR responses was very low.

$$H_{i,j} = 0.3237 m_{i,j} \qquad 12$$

$$m_{i,j} = \frac{H_{i,j}}{0.3237} \qquad 13$$

Equation 13 enables to calculate $m_{i,j,}$ i.e., the mass of the polymer in an element $E_{i,j}$ of the matrix (i.e., in volume of one LAC fraction = 100 $\mu$L), when an IR response ($H_{i,j}$) for that element is known. The Limit of Quantification (LOQ) was calculated by determining the signal to noise ratio at lower concentrations. A signal to noise ratio of ~ 10 corresponds to the LOQ.[154] The LOQ for the IR4 detector was calculated as 0.03 mg/mL.

The relation between the SEC elution volume and the molar mass at peak maximum ($M_p$) was obtained by analyzing PE standards (dissolved in TCB) with the SEC column.

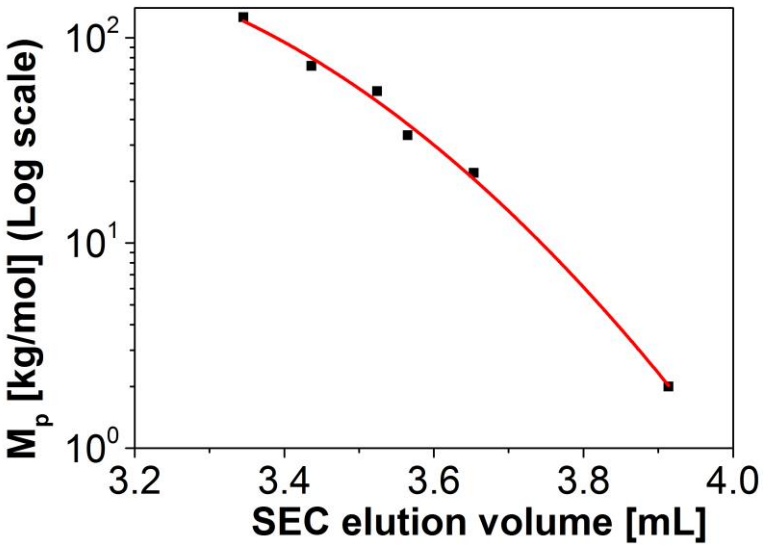



*Figure 32. Calibration of the SEC separation with PE standards obtained with HT-SEC/IR4 ($IR_1$ signal): the $M_p$ of PE standards versus elution volume. Concentration: 2 mg/mL. SEC solvent flow rate: 2.5 mL/min.*

The calibration of the SEC separation is presented in Figure 32 and is expressed with Equation 14 ($R_2$ = 0.993):

$$M_p = 14.33(V_{SEC}) - 2.4(V_{SEC})^2 - 15.95 \qquad 14$$

With the aim to calibrate the LAC separation, three copolymer samples and one PE standard (Table 5) were analyzed by HT 2D-LC at optimized chromatographic conditions (Method No. 2 in Table 3). The relation between the LAC elution volume at peak maximum ($E_{pmax}$) with respect to the average chemical composition of the EP copolymers is illustrated in Figure 33.

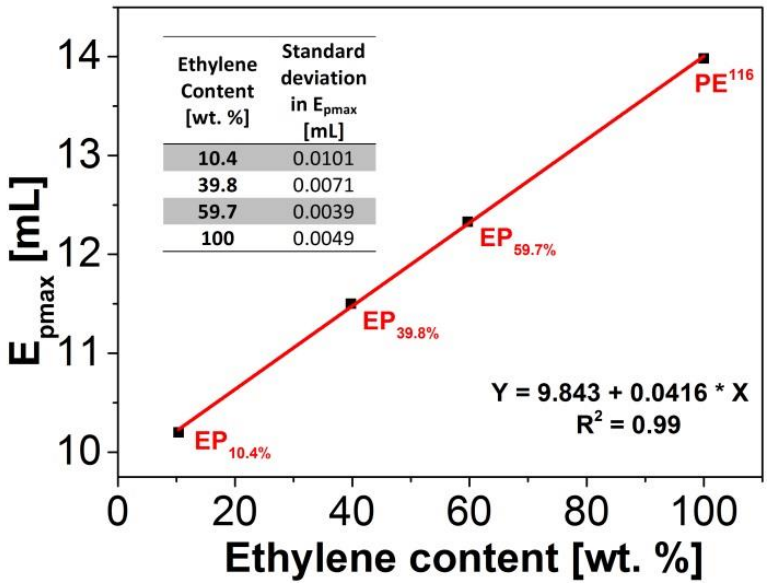



*Figure 33. Calibration of the LAC separation obtained with HT 2D-LC/IR4 ($IR_1$ signal): $E_{pmax}$ versus the average chemical composition of the EP copolymers.*

A linear relationship between the LAC elution volume ($E_{pmax}$) and the ethylene content was obtained (Figure 33) which can be expressed as Equation 16. The reproducibility of the results was checked by injecting each sample three times and the standard deviation in $E_{pmax}$ for each sample is shown in Figure 33.

$$E_{p\max} = 9.843 + 0.0416(EC) \qquad 15$$

$$EC = \frac{(E_{p\max} - 9.843)}{0.0416} \qquad 16$$

where EC represents the ethylene content in wt. % in an EP copolymer.

Applying the three calibrations (Figure 31-33, Equations 13, 14, 16), the mass fraction of polymer, the $M_p$ and the weight average ethylene content ($EC_w$) related to the LAC fractions (Figure 29c) of sample $EP_{59.7}$ (fraction 113 – 129) were calculated and the results are summarized in Table 9.

*Table 9. $M_p$, $EC_w$ and mass of polymer for the LAC fractions of sample $EP_{59.7}$.*

| Number of fraction | $M_p$ [kg/mol] | $EC_w$ [wt. %] | Mass fraction [wt. %] |
|---|---|---|---|
| 113 | 32.4 | 35.0 | 1.0 |
| 114 | 49.8 | 37.4 | 1.7 |
| 115 | 59.1 | 39.8 | 2.1 |
| 116 | 73.5 | 42.2 | 3.1 |
| 117 | 67.9 | 44.6 | 4.1 |
| 118 | 48.2 | 47.0 | 5.9 |
| 119 | 64.9 | 49.5 | 6.8 |
| 120 | 71.2 | 51.9 | 9.6 |
| 121 | 74.6 | 54.3 | 11.8 |
| 122 | 77.5 | 56.7 | 17.2 |
| 123 | 79.3 | 59.1 | 17.6 |
| 124 | 77.9 | 61.5 | 13.3 |
| 125 | 95.4 | 63.9 | 4.2 |
| 126 | 160.9 | 66.3 | 1.5 |
| 127 | 251.9 | 68.7 | 0.1 |

The results in Table 9 show that the initial fractions from the LAC column have a lower $M_w$ compared to the later fractions and that most of the polymer sample eluted in the middle fractions.

### 5.3.5 Matrix corresponding to a contour plot

The data presented in the form of matrices enable to perform mathematical operations with the aim to investigate differences in the molecular heterogeneities of polymers in a quantitative manner, which is not possible with the contour plots. Using the calibrations illustrated in Figure 32 and Figure 33 i.e., Equations 14 and 16, the x- and y-axis were translated for the contour plots of $EP_{59.7}$ and $EP_{39.8}$. In the same sense the IR response (z-axis) was also translated to the mass of polymer using Equation 13.

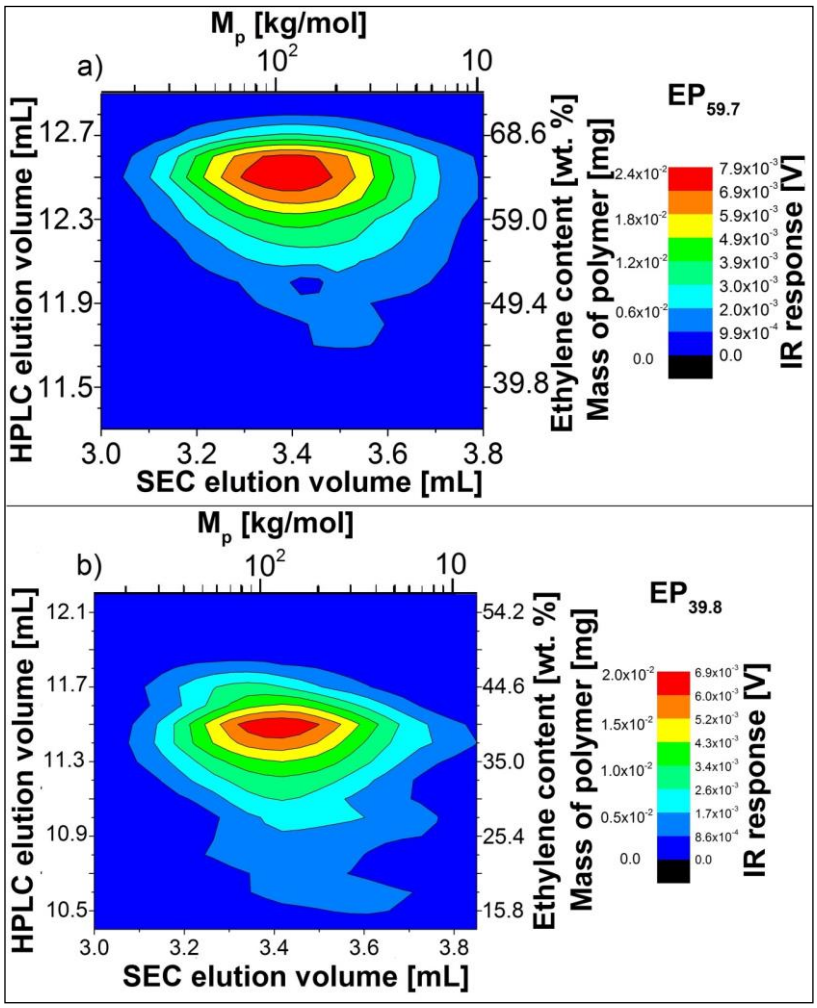
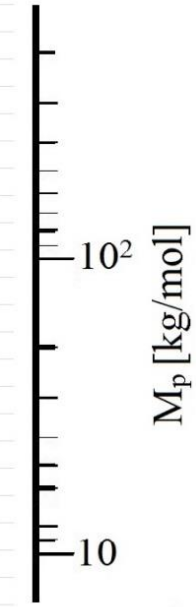



*Figure 34. Color coded contour plots for a) sample $EP_{59.7}$ and b) $EP_{39.8}$. Concentration: 2 mg/mL. 2D-LC method No. 2 was used (Table 3).*

The data used for creation of these contour plots (Figure 34) are shown in the form of matrices. The number of rows in the matrices (x-axis of the contour plot) corresponds to the number of points (IR-response) from one SEC analysis, and the number of columns (y-axis of the contour plot) corresponds to the number of fractions from the LAC column in Figure 35.

HPLC elution volume [mL]

| SEC elution volume [mL] | 11.4 | 11.5 | 11.6 | 11.7 | 11.8 | 11.9 | 12 | 12.1 | 12.2 | 12.3 | 12.4 | 12.5 | 12.6 | 12.7 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3.03 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 3.07 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.004 | 0.003 | 0 | 0 |
| 3.11 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.003 | 0.004 | 0.007 | 0.006 | 0 | 0 |
| 3.15 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.005 | 0.006 | 0.01 | 0.008 | 0 | 0 |
| 3.19 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.004 | 0.007 | 0.009 | 0.013 | 0.011 | 0.004 | 0 |
| 3.23 | 0 | 0 | 0 | 0 | 0 | 0 | 0.004 | 0.005 | 0.008 | 0.012 | 0.016 | 0.015 | 0.006 | 0 |
| 3.26 | 0 | 0 | 0 | 0 | 0 | 0 | 0.005 | 0.007 | 0.01 | 0.014 | 0.019 | 0.017 | 0.007 | 0 |
| 3.3 | 0 | 0 | 0 | 0 | 0 | 0.003 | 0.006 | 0.008 | 0.012 | 0.017 | 0.022 | 0.02 | 0.008 | 0 |
| 3.34 | 0 | 0 | 0 | 0 | 0.003 | 0.004 | 0.006 | 0.009 | 0.013 | 0.019 | 0.024 | 0.021 | 0.009 | 0 |
| 3.38 | 0 | 0 | 0 | 0 | 0.004 | 0.004 | 0.007 | 0.01 | 0.013 | 0.02 | 0.024 | 0.022 | 0.01 | 0 |
| 3.42 | 0 | 0 | 0 | 0 | 0.004 | 0.002 | 0.007 | 0.01 | 0.014 | 0.02 | 0.024 | 0.022 | 0.01 | 0 |
| 3.46 | 0 | 0 | 0.003 | 0.003 | 0.004 | 0.002 | 0.007 | 0.01 | 0.013 | 0.019 | 0.023 | 0.021 | 0.009 | 0 |
| 3.49 | 0 | 0 | 0.003 | 0.004 | 0.004 | 0.006 | 0.007 | 0.01 | 0.012 | 0.018 | 0.021 | 0.019 | 0.008 | 0 |
| 3.53 | 0 | 0 | 0.003 | 0.004 | 0.003 | 0.005 | 0.006 | 0.009 | 0.011 | 0.016 | 0.018 | 0.017 | 0.007 | 0 |
| 3.57 | 0 | 0 | 0 | 0.003 | 0 | 0.005 | 0.006 | 0.008 | 0.009 | 0.014 | 0.015 | 0.015 | 0.006 | 0 |
| 3.61 | 0 | 0 | 0 | 0 | 0 | 0.004 | 0.005 | 0.007 | 0.008 | 0.011 | 0.012 | 0.012 | 0.004 | 0 |
| 3.65 | 0 | 0 | 0 | 0 | 0 | 0.004 | 0.004 | 0.006 | 0.006 | 0.009 | 0.01 | 0.009 | 0.003 | 0 |
| 3.69 | 0 | 0 | 0 | 0 | 0 | 0.003 | 0.004 | 0.004 | 0.005 | 0.007 | 0.007 | 0.007 | 0 | 0 |
| 3.72 | 0 | 0 | 0 | 0 | 0 | 0 | 0.003 | 0.003 | 0.004 | 0.005 | 0.005 | 0.005 | 0 | 0 |
| 3.76 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.004 | 0.004 | 0.004 | 0 | 0 |
| 3.8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 3.84 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | 37.4 | 39.8 | 42.2 | 44.6 | 47 | 49.4 | 51.8 | 54.2 | 56.6 | 59 | 61.4 | 63.8 | 66.2 | 68.6 |

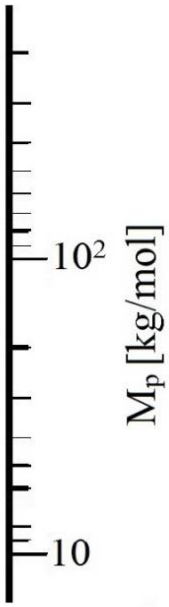



a) Ethylene content in EP copolymer [wt. %]

Note: Numbers in the matrix represent mass of the polymer in each element (in mg).

HPLC elution volume [mL]

| SEC elution volume [mL] | 10.7 | 10.8 | 10.9 | 11 | 11.1 | 11.2 | 11.3 | 11.4 | 11.5 | 11.6 | 11.7 | 11.8 | 11.9 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3.03 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 3.07 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 3.11 | 0 | 0 | 0 | 0 | 0 | 0 | 0.003 | 0.004 | 0.004 | 0 | 0 | 0 | 0 |
| 3.15 | 0 | 0 | 0 | 0 | 0 | 0 | 0.005 | 0.006 | 0.006 | 0.004 | 0.004 | 0 | 0 |
| 3.19 | 0 | 0 | 0 | 0 | 0 | 0.004 | 0.006 | 0.009 | 0.009 | 0.005 | 0.005 | 0 | 0 |
| 3.23 | 0 | 0 | 0 | 0 | 0.003 | 0.006 | 0.008 | 0.011 | 0.012 | 0.007 | 0.007 | 0.004 | 0 |
| 3.26 | 0 | 0 | 0 | 0 | 0.004 | 0.007 | 0.01 | 0.013 | 0.015 | 0.009 | 0.008 | 0.004 | 0 |
| 3.3 | 0 | 0 | 0.003 | 0.003 | 0.006 | 0.008 | 0.011 | 0.015 | 0.018 | 0.011 | 0.009 | 0.004 | 0 |
| 3.34 | 0 | 0.004 | 0.004 | 0.005 | 0.007 | 0.009 | 0.012 | 0.017 | 0.02 | 0.012 | 0.009 | 0.004 | 0 |
| 3.38 | 0 | 0.004 | 0.005 | 0.006 | 0.008 | 0.01 | 0.013 | 0.018 | 0.021 | 0.013 | 0.009 | 0.004 | 0 |
| 3.42 | 0 | 0.004 | 0.005 | 0.006 | 0.008 | 0.01 | 0.013 | 0.018 | 0.021 | 0.014 | 0.008 | 0.003 | 0 |
| 3.46 | 0 | 0.004 | 0.005 | 0.006 | 0.008 | 0.01 | 0.013 | 0.017 | 0.021 | 0.013 | 0.007 | 0.003 | 0 |
| 3.49 | 0 | 0.004 | 0.004 | 0.006 | 0.007 | 0.009 | 0.012 | 0.016 | 0.019 | 0.012 | 0.006 | 0 | 0 |
| 3.53 | 0 | 0.004 | 0.004 | 0.006 | 0.006 | 0.008 | 0.011 | 0.014 | 0.017 | 0.01 | 0.005 | 0 | 0 |
| 3.57 | 0 | 0 | 0.004 | 0.006 | 0.005 | 0.007 | 0.01 | 0.012 | 0.015 | 0.009 | 0.004 | 0 | 0 |
| 3.61 | 0 | 0 | 0.003 | 0.005 | 0.004 | 0.006 | 0.008 | 0.01 | 0.012 | 0.007 | 0 | 0 | 0 |
| 3.65 | 0 | 0 | 0.003 | 0.005 | 0.004 | 0.005 | 0.007 | 0.008 | 0.01 | 0.006 | 0 | 0 | 0 |
| 3.69 | 0 | 0 | 0 | 0.004 | 0 | 0.003 | 0.005 | 0.007 | 0.008 | 0.004 | 0 | 0 | 0 |
| 3.72 | 0 | 0 | 0 | 0.004 | 0 | 0 | 0.004 | 0.006 | 0.006 | 0 | 0 | 0 | 0 |
| 3.76 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.005 | 0.005 | 0 | 0 | 0 | 0 |
| 3.8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.004 | 0.003 | 0 | 0 | 0 | 0 |
| 3.84 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | 21.6 | 23 | 25.4 | 27.8 | 30.2 | 32.6 | 35 | 37.4 | 39.8 | 42.2 | 44.6 | 47 | 49.4 |




b) Ethylene content in EP copolymer [wt. %]

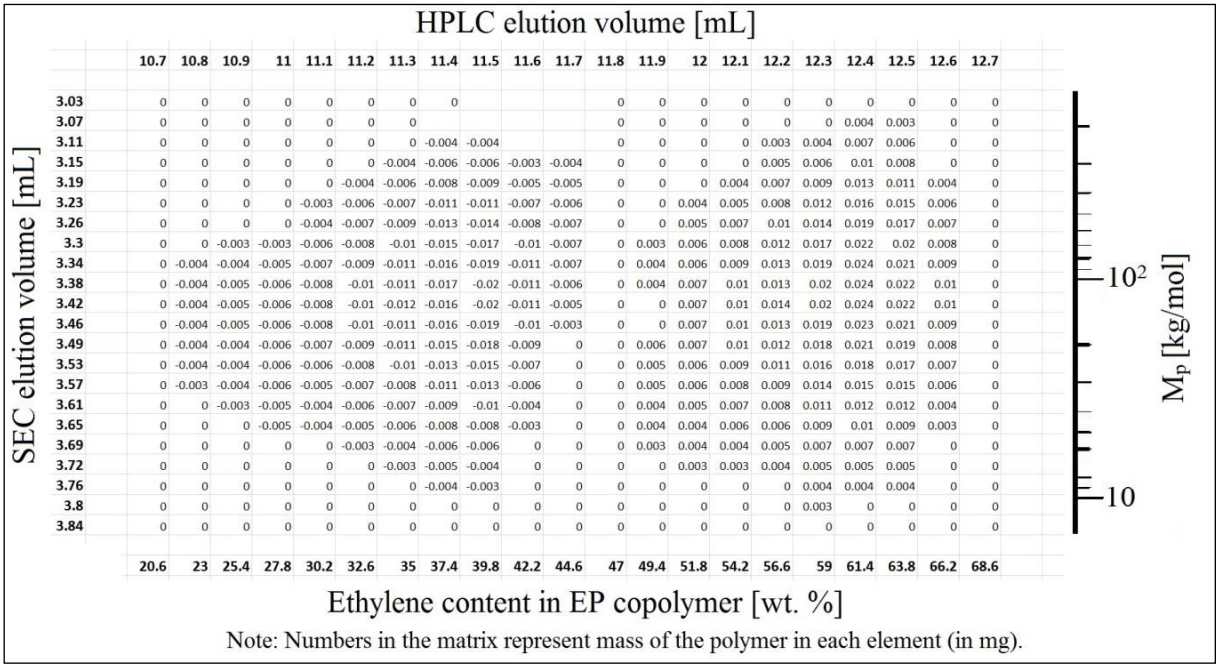
Note: Numbers in the matrix represent mass of the polymer in each element (in mg).

*Figure 35. Matrix corresponding to the 2D-contour plots (for Figure 34): a) sample $EP_{59.7}$ and b) $EP_{39.8}$.*

The matrices shown in Figure 35 contain the quantitative data, and the mass of EP copolymer for a particular coordinate of chemical composition and molar mass can be identified from the matrix.

### 5.3.6 Application of the matrix approach

The EP copolymers of varying average ethylene content can also contain identical segments i.e., ensembles of macromolecules which are identical with regard to their average molar mass and chemical composition. Samples $EP_{39.8}$ and $EP_{59.7}$ were analyzed using HT 2D-LC/IR. The matrix corresponding to the contour plot for sample $EP_{39.8}$ (Figure 35b) was subtracted from the matrix corresponding to the contour plot of sample $EP_{59.7}$ (Figure 35a) to obtain information about the common segments of the two copolymers. The difference matrix is shown in Figure 36 and the relief plots generated from this (for unique and identical segments in $EP_{39.8}$ and $EP_{59.7}$) are shown in Figure 37 and Figure 38.




| | 10.7 | 10.8 | 10.9 | 11 | 11.1 | 11.2 | 11.3 | 11.4 | 11.5 | 11.6 | 11.7 | 11.8 | 11.9 | 12 | 12.1 | 12.2 | 12.3 | 12.4 | 12.5 | 12.6 | 12.7 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3.03 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | | | | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 3.07 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | | | | | 0 | 0 | 0 | 0 | 0 | 0 | 0.004 | 0.003 | 0 | 0 |
| 3.11 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -0.004 | -0.004 | | | 0 | 0 | 0 | 0 | 0.003 | 0.004 | 0.007 | 0.006 | 0 | 0 |
| 3.15 | 0 | 0 | 0 | 0 | 0 | 0 | -0.004 | -0.006 | -0.006 | -0.003 | -0.004 | 0 | 0 | 0 | 0 | 0.005 | 0.006 | 0.01 | 0.008 | 0 | 0 |
| 3.19 | 0 | 0 | 0 | 0 | 0 | -0.004 | -0.006 | -0.008 | -0.009 | -0.005 | -0.005 | 0 | 0 | 0 | 0.004 | 0.007 | 0.009 | 0.013 | 0.011 | 0.004 | 0 |
| 3.23 | 0 | 0 | 0 | 0 | -0.003 | -0.006 | -0.007 | -0.011 | -0.011 | -0.007 | -0.006 | 0 | 0 | 0.004 | 0.005 | 0.008 | 0.012 | 0.016 | 0.015 | 0.006 | 0 |
| 3.26 | 0 | 0 | 0 | 0 | -0.004 | -0.007 | -0.009 | -0.013 | -0.014 | -0.008 | -0.007 | 0 | 0 | 0.005 | 0.007 | 0.01 | 0.014 | 0.019 | 0.017 | 0.007 | 0 |
| 3.3 | 0 | 0 | -0.003 | -0.003 | -0.006 | -0.008 | -0.01 | -0.015 | -0.017 | -0.01 | -0.007 | 0 | 0.003 | 0.006 | 0.008 | 0.012 | 0.017 | 0.022 | 0.02 | 0.008 | 0 |
| 3.34 | 0 | -0.004 | -0.004 | -0.005 | -0.007 | -0.009 | -0.011 | -0.016 | -0.019 | -0.011 | -0.007 | 0 | 0.004 | 0.006 | 0.009 | 0.013 | 0.019 | 0.024 | 0.021 | 0.009 | 0 |
| 3.38 | 0 | -0.004 | -0.005 | -0.006 | -0.008 | -0.01 | -0.011 | -0.017 | -0.02 | -0.011 | -0.006 | 0 | 0.004 | 0.007 | 0.01 | 0.013 | 0.02 | 0.024 | 0.022 | 0.01 | 0 |
| 3.42 | 0 | -0.004 | -0.005 | -0.006 | -0.008 | -0.01 | -0.012 | -0.016 | -0.02 | -0.011 | -0.005 | 0 | 0 | 0.007 | 0.01 | 0.014 | 0.02 | 0.024 | 0.022 | 0.01 | 0 |
| 3.46 | 0 | -0.004 | -0.005 | -0.006 | -0.008 | -0.01 | -0.011 | -0.016 | -0.019 | -0.01 | -0.003 | 0 | 0 | 0.007 | 0.01 | 0.013 | 0.019 | 0.023 | 0.021 | 0.009 | 0 |
| 3.49 | 0 | -0.004 | -0.004 | -0.006 | -0.007 | -0.009 | -0.011 | -0.015 | -0.018 | -0.009 | 0 | 0 | 0.006 | 0.007 | 0.01 | 0.012 | 0.018 | 0.021 | 0.019 | 0.008 | 0 |
| 3.53 | 0 | -0.004 | -0.004 | -0.006 | -0.006 | -0.008 | -0.01 | -0.013 | -0.015 | -0.007 | 0 | 0 | 0.005 | 0.006 | 0.009 | 0.011 | 0.016 | 0.018 | 0.017 | 0.007 | 0 |
| 3.57 | 0 | -0.003 | -0.004 | -0.006 | -0.005 | -0.007 | -0.008 | -0.011 | -0.013 | -0.006 | 0 | 0 | 0.005 | 0.006 | 0.008 | 0.009 | 0.014 | 0.015 | 0.015 | 0.006 | 0 |
| 3.61 | 0 | 0 | -0.003 | -0.005 | -0.004 | -0.006 | -0.007 | -0.009 | -0.01 | -0.004 | 0 | 0 | 0.004 | 0.005 | 0.007 | 0.008 | 0.011 | 0.012 | 0.012 | 0.004 | 0 |
| 3.65 | 0 | 0 | 0 | -0.005 | -0.004 | -0.005 | -0.006 | -0.008 | -0.008 | -0.003 | 0 | 0 | 0.004 | 0.004 | 0.006 | 0.006 | 0.009 | 0.01 | 0.009 | 0.003 | 0 |
| 3.69 | 0 | 0 | 0 | 0 | 0 | -0.003 | -0.004 | -0.006 | -0.006 | 0 | 0 | 0 | 0.003 | 0.004 | 0.004 | 0.005 | 0.007 | 0.007 | 0.007 | 0 | 0 |
| 3.72 | 0 | 0 | 0 | 0 | 0 | 0 | -0.003 | -0.005 | -0.004 | 0 | 0 | 0 | 0 | 0.003 | 0.003 | 0.004 | 0.005 | 0.005 | 0.005 | 0 | 0 |
| 3.76 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | -0.004 | -0.003 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.004 | 0.004 | 0.004 | 0 | 0 |
| 3.8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.003 | 0 | 0 | 0 | 0 |
| 3.84 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | 20.6 | 23 | 25.4 | 27.8 | 30.2 | 32.6 | 35 | 37.4 | 39.8 | 42.2 | 44.6 | 47 | 49.4 | 51.8 | 54.2 | 56.6 | 59 | 61.4 | 63.8 | 66.2 | 68.6 |

*Figure 36. Matrix obtained after subtraction operation ($EP_{59.7}$ – $EP_{39.8}$). 2D-LC method no. 2 was used (Table 3).*

Note: Negative values in the matrix show the unique segments in sample $EP_{39.8}$ and positive values show the unique segments in $EP_{59.7}$.

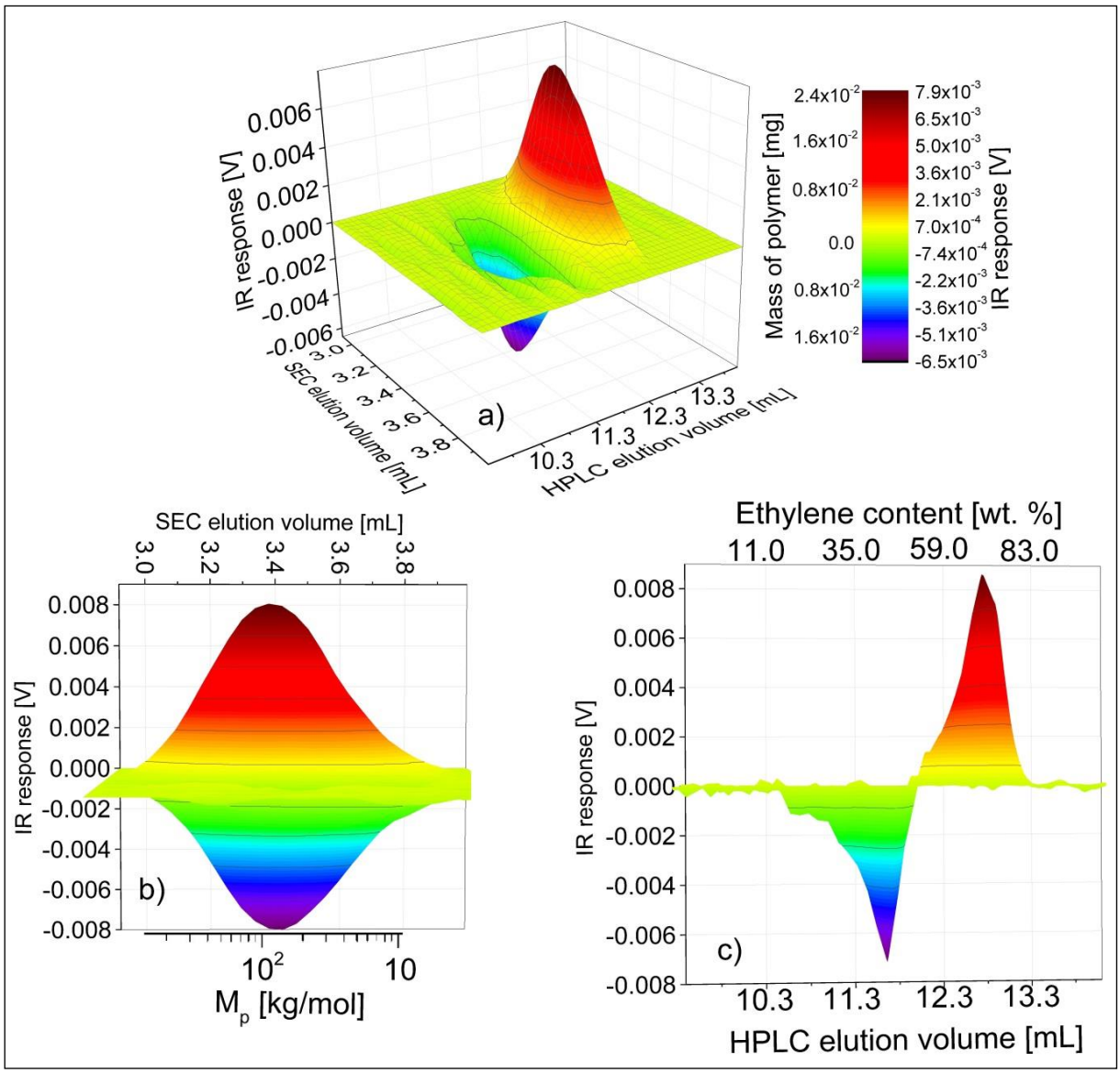



*Figure 37. Plots obtained after subtraction ($EP_{59.7}$ – $EP_{39.8}$) showing unique segments in both the copolymers: a) Three dimensional surface plot, b) Projection of the SEC elution and c) Projection of the LAC elution. Note: Negative peaks in the figures correspond to the unique segments in $EP_{39.8}$ and the positive peaks indicate the unique segments in $EP_{59.7}$.*

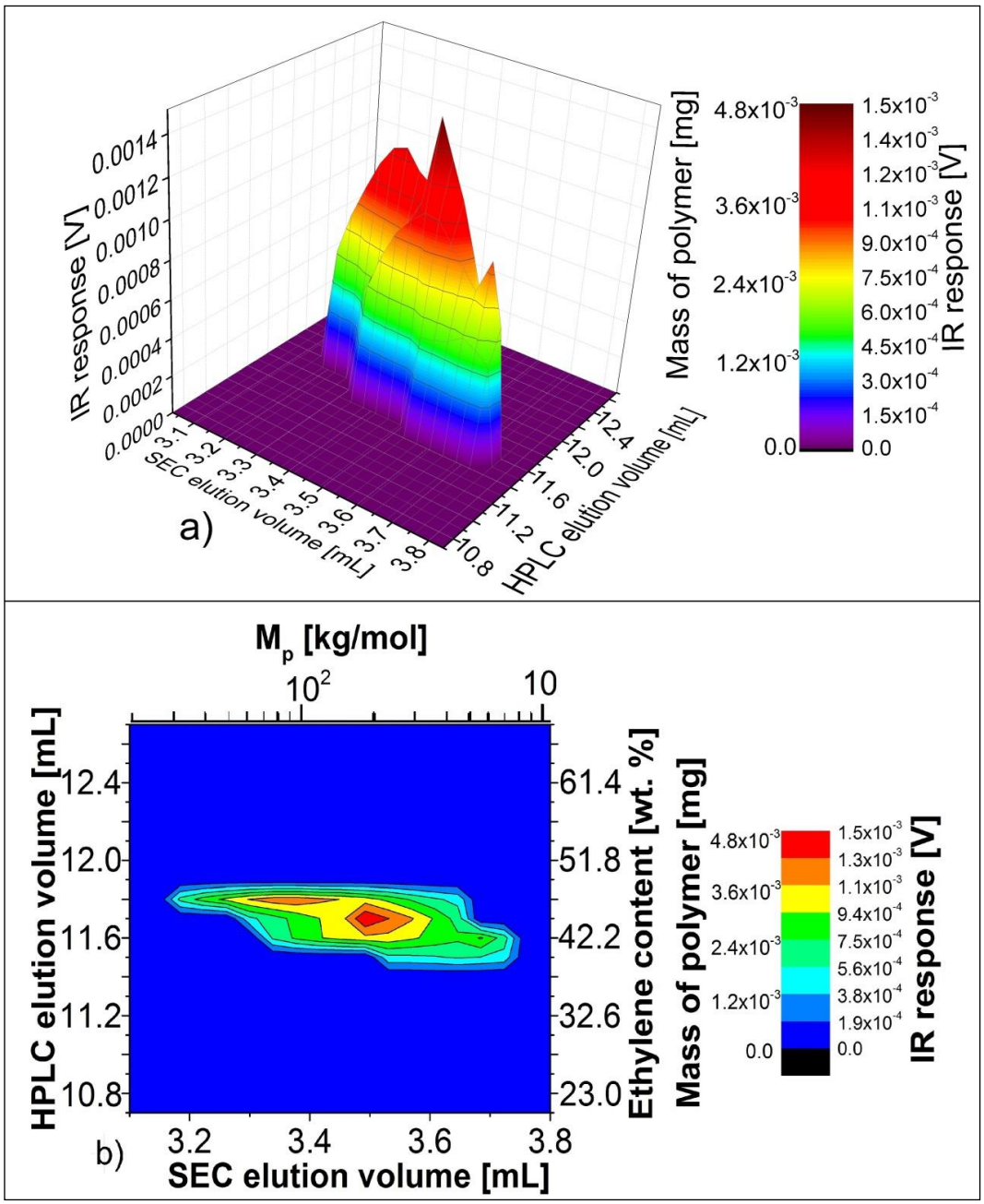



*Figure 38. Plots obtained after subtraction ($EP_{59.7}$ – $EP_{39.8}$) showing the identical segments in both copolymers: a) Relief plot, b) Two dimensional contour plot.*

The matrix in Figure 36 shows negative values (shortage part) for the part present only in $EP_{39.8}$, and positive values (surplus part) for the part present only in $EP_{59.7}$. The copolymers contained identical segments, which are not visible in the matrix (Figure 36). However, the mass fraction of the identical segments in both the

copolymers can be calculated by using the data from the matrices corresponding to their contour plots (Figure 35) and the data from the subtraction matrix (Figure 36).

It is valid that the mass of sample $EP_{39.8}$ can be calculated from the corresponding matrix as sum of identical segments with the mass $m_I$ and unique segments with the mass $D_1$:

$$m_1 = D_1 + m_I \quad (17)$$

An analogue equation may be written for $EP_{59.7}$:

$$m_2 = D_2 + m_I \quad (18)$$

where $m_2$ may be calculated from the corresponding matrix.

The mass of both samples ($m_T$) can be obtained after summation of both matrices using Equation 19:

$$m_T = m_1 + m_2 = D_1 + D_2 + 2m_I \quad (19)$$

while the difference mass ($m_D$) can be calculated from the subtraction of matrices:

$$m_D = m_1 - m_2 = D_1 + D_2 \quad (20)$$

Finally, the mass of the identical segments ($m_I$) in both the samples can be calculated using Equation 21:

$$m_I = \frac{m_T - m_D}{2} \quad (21)$$

Using Equation 21 the mass fraction of identical segments in both the copolymers was determined and the corresponding contour plot is shown in Figure 38. Both the samples contained 10.5 wt. % of identical segments in the compositional range 39.8 – 47.0 wt. % (ethylene content).

The number and weight average values of both the molar mass distribution ($M_n$, $M_w$) and the chemical composition distribution ($EC_n$, $EC_w$) were calculated using Equations 22 - 25 as described by Kebritchi et al.[155] The $M_{i,j}$ and the $H_{i,j}$ values were obtained from the corresponding matrices.

$$M_n = \frac{\sum M_{i,j} H_{i,j}}{\sum H_{i,j}} \quad (22)$$

$$M_w = \frac{\sum M_{i,j}^2 H_{i,j}}{\sum M_{i,j} H_{i,j}} \quad (23)$$

$$EC_n = \frac{\sum EC_{i,j} H_{i,j}}{\sum H_{i,j}} \quad (24)$$

$$EC_w = \frac{\sum EC_{i,j}^2 H_{i,j}}{\sum EC_{i,j} H_{i,j}} \quad (25)$$

The calculated average molar mass (M) and average ethylene content (EC) of the identical and unique segments are summarized in Table 10.

*Table 10. Average molar mass and average chemical composition of the identical and unique segments identified in two polymer samples.*

| **Polymer sample** | **$EP_{59.7}$** | | | | **$EP_{39.8}$** | | | |
|---|---|---|---|---|---|---|---|---|
| Segments | Identical | | Unique | | Identical | | Unique | |
| | | | | | | | | |
| Mass fraction [wt. %] | 10.5 | | 89.5 | | 10.5 | | 89.5 | |
| | | | | | | | | |
| Average M [kg/mol] | $M_n$ | $M_w$ | $M_n$ | $M_w$ | $M_n$ | $M_w$ | $M_n$ | $M_w$ |
| | 79.6 | 112.6 | 107.1 | 141.7 | 79.6 | 112.6 | 107.6 | 147.5 |
| | | | | | | | | |
| Average EC [wt. %] | $EC_n$ | $EC_w$ | $EC_n$ | $EC_w$ | $EC_n$ | $EC_w$ | $EC_n$ | $EC_w$ |
| | 44.3 | 44.5 | 59.6 | 59.9 | 44.3 | 44.5 | 36.1 | 36.9 |
| | | | | | | | | |

The data in Table 10 reveal that the identical segments in both polymers have a lower average molar mass compared to the unique parts. The unique segments in $EP_{59.7}$ show a larger average ethylene content, while the unique segments of $EP_{39.8}$ have lower average ethylene content in comparison with the identical segments.

The matrix approach enables to quantify the identical and the unique segments within a pair of polymers. In this way differences in both CCD and MMD of complex polymer samples may be quantitatively visualized, evaluated and compared. Such quantitative

data about differences in the molecular heterogeneities are an important step towards establishing structure-property relationships.

### 5.4 New sorbents for HT-LAC of polyolefins – BN and $MoS_2$

Thermal Gradient Interaction Chromatography (TGIC) using reverse phase columns can be used to analyze copolymers, as shown by Chang et al.[156] and Cong et al.[16] TGIC was used to analyze the CCD of Ethylene-Octene (EO) copolymers using a Hypercarb™ column.[16] Monrabal et al.[157] showed a comparison between the TGIC profiles of a series of EO copolymers for various types of layered Atomic Level Flat Surface (ALFS) sorbents e.g., Boron Nitride (BN), Molybdenum Disulfide ($MoS_2$). BN and $MoS_2$ showed adsorption and selectivity for EO-copolymers being similar to Hypercarb™.[99]

However, the separation of polyolefins using ALFS adsorbents as a stationary phase in HT-LAC was yet not studied. The use of these ALFS adsorbents (BN and $MoS_2$) as stationary phase in HT-LAC of polyolefins will be discussed in this work. Mobile phases used for the separation of polyolefins using HT-LAC and Hypercarb™ as stationary phase have already been published.[9,152] Adsorption promoting liquids (e.g., 2E1H, n-decane, decalin and diisobutylketone) with different polarity are chosen for testing them for HT-LAC of polyolefins (e.g., *it*-PP, *st*-PP, *at*-PP and PE) with BN and $MoS_2$ as stationary phases, and the results are compared with those from Hypercarb™. Polyolefin samples will be dissolved in adsorption promoting solvent (2E1H) and analyzed using HT-LAC. Overlays of the chromatograms corresponding to different polyolefins (mobile phase: 2E1H/ TCB) are shown in Figure 39.

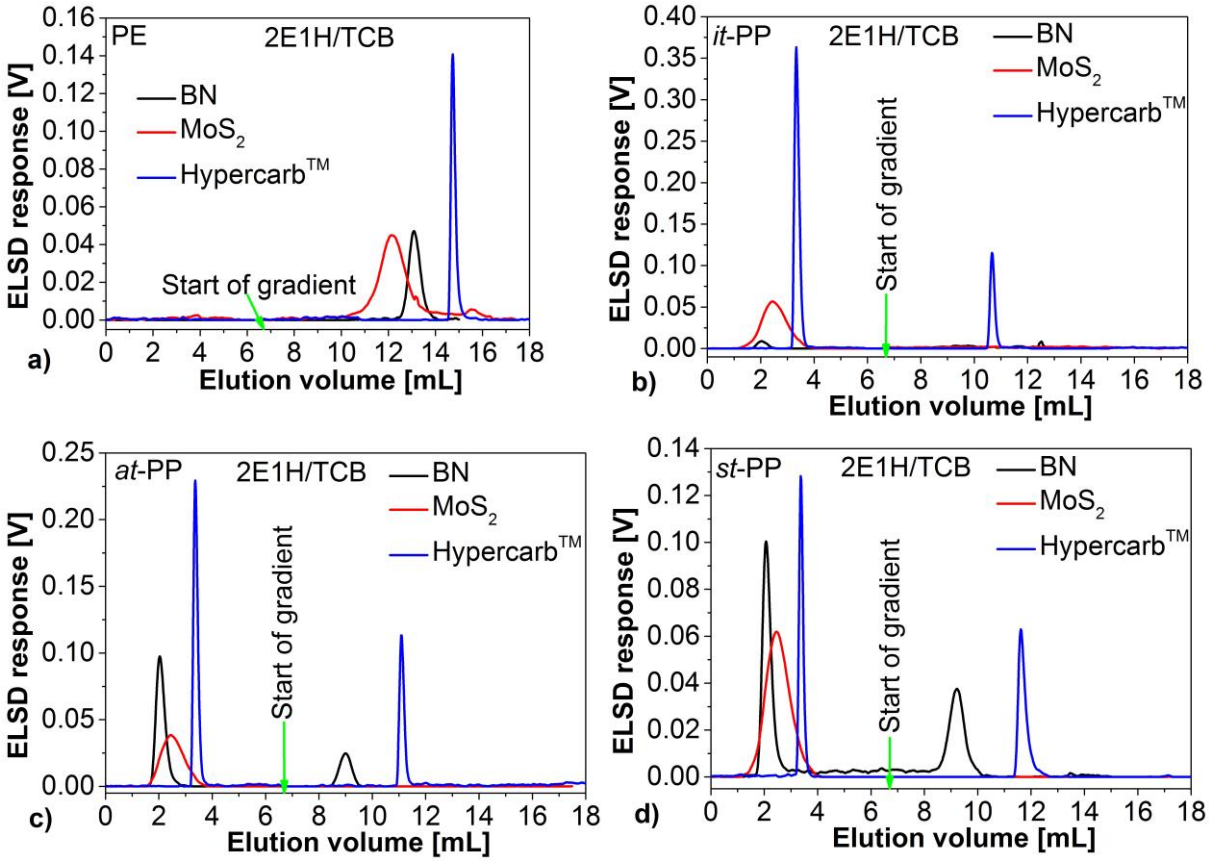



*Figure 39. Overlays of chromatograms for different polyolefin samples in 2E1H/TCB and different sorbents. Polyolefins: a) PE[181], b) it-PP[250], c) at-PP[315] and d) st-PP[174]. Gradient program as shown in Table 1 was used.*

Figure 39a shows that PE with higher $M_w$ was adsorbed on all the sorbents from mobile phase 2E1H and only eluted after the start of gradient. *it*-PP with higher $M_w$ was partially adsorbed on Hypercarb™ and it did not adsorb on the other two sorbents (Figure 39b). Both *at*-PP and *st*-PP with higher $M_w$ were partially adsorbed on Hypercarb™ and BN, but did not adsorb on $MoS_2$ (Figure 39c, d). To study the effect of molar mass on the adsorption on different sorbents more systematically varying molar masses of PE, *it*-PP and *at*-PP were dissolved in the adsorption promoting solvent (2E1H) and analyzed applying a solvent gradient. The results

obtained from these analyses (corresponding to different sorbents) are shown in Figure 40.

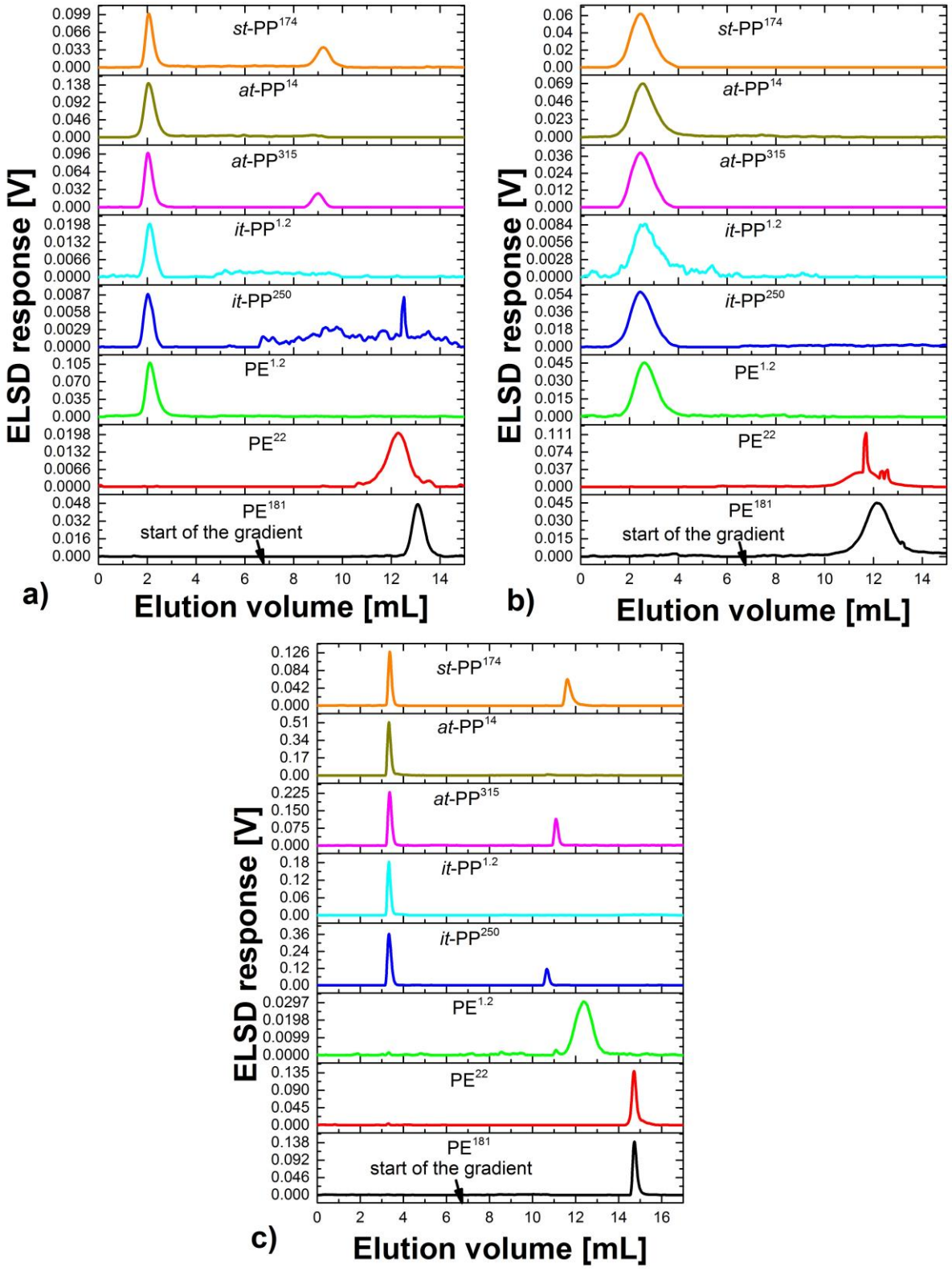


*Figure 40. Stack plots of chromatograms for different polyolefins (different molar masses) in 2E1H/TCB: a) BN, b) $MoS_2$ and c) Hypercarb™.*

It was observed that the samples with lower $M_w$ were not adsorbing on these sorbents (Figure 40) from the tested mobile phase system, which was also observed by Chitta et al. for the case of Hypercarb™. Similar to 2E1H/TCB, the separation of these samples was studied in other mobile phases i.e., n-decane/TCB, decalin/TCB and diisobutylketone/TCB. The adsorption behavior of the PE and PP's on different sorbents in different mobile phases is summarized in Table 11.

*Table 11. Adsorption behavior of the polyolefins in different sorbents/solvents at 160 °C.*

| **Polyolefin** → | **PE** | | | ***it*-PP** | | ***at*-PP** | | ***st*-PP** |
|---|---|---|---|---|---|---|---|---|
| **Sorbents/solvents** ↓ | **High $M_w$** | **Medium $M_w$** | **Low $M_w$** | **High $M_w$** | **Low $M_w$** | **High $M_w$** | **Low $M_w$** | **High $M_w$** |
| Hypercarb™ 2E1H/TCB | A | A | A | P | E | P | E | P |
| BN 2E1H/TCB | A | A | E | P | E | P | E | P |
| $MoS_2$ 2E1H/TCB | A | A | E | E | E | E | E | E |
| Hypercarb™ n-decane/TCB | A | A | P | P | E | P | E | P |
| BN n-decane/TCB | A | P | E | E | E | P | E | P |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $MoS_2$ n-decane/TCB | A | A | E | E | E | E | E | E |
| Hypercarb™ decalin/TCB | P | P | P | P | E | P | E | P |
| BN decalin/TCB | A | P | E | E | E | E | E | E |
| $MoS_2$ decalin/TCB | P | P | E | E | E | E | E | E |
| Hypercarb™ diisobutylketone/TCB | A | A | P | E | P | P | P | A |
| BN diisobutylketone/TCB | A | A | P | P | E | P | P | P |
| $MoS_2$ diisobutylketone/TCB | A | A | P | E | E | P | E | P |

P → partially adsorbed, A → fully adsorbed and E → fully eluted before the start of gradient

The measurements confirmed that BN and $MoS_2$ interact with PE and PP i.e., PE and PP may be reversibly adsorbed and desorbed from these column packings. One possible reason behind the weaker adsorption in the case of BN and $MoS_2$ might be a lower available surface area for adsorption. The order of elution in case of these sorbents (*it*-PP < *at*-PP < *st*-PP < PE) has also been found to be similar to the

Hypercarb™ in the tested mobile phases. The order of selectivity (most to least) among these sorbents was observed as: Hypercarb™ > BN > $MoS_2$.

# 6 Conclusions

The critical conditions for Isotactic Polypropylene (*it*-PP) and Syndiotactic Polypropylene (*st*-PP) have been determined for the first time in binary mobile phases (2-octanol/1,2,4-trichlorobenzene (TCB), 2-ethyl-1-hexanol (2E1H)/TCB, 2-octanol/ 1,2-dichlorobenzene (ODCB) or 2E1H/ODCB) using porous graphitic carbon as stationary phase. These critical conditions were determined using three different methods, namely according to Bashir, Cools and the classical Size Exclusion Chromatography – Liquid Adsorption Chromatography (SEC-LAC) plot. The results obtained from these three methods are in good agreement with each other. The desorption promoting solvent TCB was found to be a stronger eluent compared to ODCB, and 2-octanol was classified as weaker adsorption promoting in comparison to 2E1H. The influence of temperature on the critical conditions for *it*-PP in the range of 140 °C – 180 °C was probed, and it is found that the amount of adsorption prompting solvent needed in the mobile phase at Liquid Chromatography at Critical Conditions (LCCC) is proportional to the temperature. LCCC hyphenated to SEC (LCCC x SEC) was applied to separate a model High Impact PP (M-PP-HI), using infrared (IR) spectroscopy as detection method. This enabled a quantitative deformulation into the constituents, *it*-PP and Ethylene-Propylene (EP) copolymer, using IR detection. M-PP-HI (components in 1/1 wt. % ratio) was analyzed using LCCC x SEC and its components were baseline separated. The ratio of quantities obtained from the contour plot was 1.01/1 wt. % of *it*-PP/EP, which reflected the injected amount of these components in M-PP-HI.

Limited recovery of analyzed polymers is usually problematic in LCCC, which may lead to serious errors while applying LCCC. A new method for determination of the

critical conditions was elaborated and experimentally tested. This method requires only one high molar mass polymer sample, which is injected in varying mobile phase compositions in LAC mode. After elution of the polymer from the column, its recovery is checked by pumping pure desorption promoting solvent. The first composition of the mobile phase at which the polymer eluted with full recovery (i.e., no peak of polymer appeared in the chromatogram after pumping pure desorption promoting solvent) corresponds to the critical conditions. An advantage of this method is that conditions for LCCC of a polymer can be identified with a single high molar mass sample. An advantage of practical nature is that no gradient pump is needed. This new method for the determination of critical conditions also reduces the sources of errors.

An Evaporative Light Scattering Detector (ELSD) is widely used with LAC, which offers the advantage of evaporating the solvents of the mobile phase. However, an ELSD cannot be used for quantitative detection as its response is non-linear with respect to the injected concentration of the analyte. On the other side filter based IR4 has been extensively used for quantitative analysis with High Temperature Size Exclusion Chromatography (HT-SEC) where an isocratic mobile phase, which is IR transparent in the detected wavelength region, is used. This detection principle may in principle also be applied to High Temperature Two Dimensional Liquid Chromatography (HT 2D-LC), where the elution in the second dimension occurs quasi-isocratic. This was probed for EP copolymer samples. The adsorption promoting solvents used in the first dimension of the HT 2D-LC are not IR transparent. Consequently, the portion of the adsorption promoting solvent injected with the transfer from the first dimension of separation to the second dimension of separation

leads to intense solvent peaks which overlapped with the peaks of polymer. This problem was solved by optimizing the solvent flow rate in the first dimension of the separation. The experimental data from 2D-LC: elution volume in LAC, elution volume in SEC and response of the IR detector were then organized into a matrix. Calibrations of the HT-LAC separation with respect to chemical composition, the HT-SEC separation with respect to molar mass and the response of IR detector with respect to mass of polymer injected were performed. A new method was developed to calibrate the IR response with respect to the mass of injected polymer (EP), which required only one injection of polymer solution (one-shot calibration method). This one shot method for calibration reduces the sources of errors, originating from preparing stock solutions and multiple injections. The Limit of Quantification (LOQ) for the IR4 detector used with HT 2D-LC/IR was calculated as 0.03 mg/mL (at signal to noise ratio of ~10).

The matrices corresponding to the contour plots may be used to determine the mass of EP copolymer of any particular chemical composition and molar mass of interest. Subtraction of matrices corresponding to different EP copolymer samples enabled to identify the identical and the unique segments present in pairs of EP samples: Summation and subtraction of both matrices were used to calculate the mass fraction of the identical segments. The Molar Mass Distribution (MMD), Chemical Composition Distribution (CCD) as well as the corresponding average values of the identical and unique segments were calculated and presented in numerical and graphical form. The described procedure opens the perspective to derive structure property relationships from HT 2D-LC results, as the differences between several polymer materials can be compared qualitatively and quantitatively with respect to one reference sample (one

sample from a set of samples of interest is chosen as a reference sample). Quantification of the common and unique segments for series of polymer samples will lead to better understand their structure-property relationships as well as the selection of catalysts and processes.

The unique selectivity of porous graphite as stationary phase as elaborated provides motivation to search for stationary phases with improved properties: Analogous to PGC, Boron Nitride (BN) and Molybdenum Sulfide ($MoS_2$) also show layered Atomic Level Flat Surface (ALFS). The adsorption behavior of Polypropylene (PP) and Polyethylene (PE) was studied on stationary phases BN and $MoS_2$, using adsorption promoting mobile phases with different polarity and the results were compared with Hypercarb™. Similar to Hypercarb™, PP and PE can be reversibly adsorbed and desorbed from these stationary phases. Yet, the influence of the molar mass on the separation and the order of elution of PP and PE with these stationary phases were observed to be similar to Hypercarb™.

## 7 References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**Publications:**

1. **Sampat Singh Bhati**, Tibor Macko, Robert Brüll, Dibyaranjan Mekap, Liquid chromatography at critical conditions of polypropylene, **Macromolecular Chemistry and Physics**, 2015, 216, p. 2179-2189
2. **Sampat Singh Bhati**, Tibor Macko, Robert Brüll, Quantification of identical and unique segments in polymers using two dimensional liquid chromatography with infra-red detection, **Polyolefins Journal**, 2016, 3, p. 119-133
3. **Sampat Singh Bhati**, Tibor Macko, Robert Brüll, Estimation of critical conditions of polymers based on monitoring the polymer recovery, **Journal of Chromatography A**, 2016, 1451, 91-96

**Oral presentations:**

1. "High-temperature high performance liquid chromatography (HT-HPLC) of polypropylene", DPI Polyolefin Cluster Meeting, March 2014, Amsterdam, The Netherlands.
2. "Comparison of IR and ELS detection in high temperature 2D-LC of high impact polypropylene", DPI Polyolefin Cluster Meeting, June 2014, Amsterdam, the Netherlands.
3. "Quantitative analysis of Ethylene-Propylene copolymers using infra-red detection in high temperature 2D-LC", DPI Polyolefin Cluster meeting, June 2015, Amsterdam, The Netherlands.
4. "Liquid chromatography at critical conditions of polypropylene", SABIC & Fraunhofer-LBF Meeting, August 2015, Darmstadt, Germany.

**Webinars:**

1. "Using infra-red detection in high temperature 2D-LC of Ethylene-Polypropylene copolymers", DPI Webinar, October 2014, Darmstadt, Germany.

**Posters:**

1. S. S. Bhati, T. Macko, R. Brüll, Calibration of high temperature HPLC separation of Ethylene-Propylene copolymers, DPI Annual Meeting, November 2013, Arnhem, The Netherlands.
2. S. S. Bhati, T. Macko, R. Brüll, Developing IR detection for the separation of polyolefins by high temperature two dimensional liquid chromatography (HT 2D-LC), DPI Annual Meeting, November 2014, Arnhem, The Netherlands.
3. S. S. Bhati, T. Macko, R. Brüll, New method for determination of critical conditions of polymers, SCM-07 Conference, January 2015, Amsterdam, The Netherlands.
4. S. S. Bhati, T. Macko, R. Brüll, Liquid chromatography under critical conditions (LCCC) of polypropylene, SCM-07 Conference, January 2015, Amsterdam, The Netherlands.
5. S. S. Bhati, T. Macko, R. Brüll, Application of liquid chromatography at critical conditions for separation of high impact PP using HT 2D-LC/IR, DPI Annual Meeting, November 2015, Arnhem, The Netherlands.
6. S. S. Bhati, T. Macko, R. Brüll, Using infrared detection in two-dimensional liquid chromatography of random ethylene-propylene copolymers, SCM-07 Conference, January 2015, Amsterdam, The Netherlands.
7. S. S. Bhati, T. Macko, R. Brüll, New liquid chromatography mode for separation of polypropylene, World Polyolefin Congress, November 2015, Tokyo, Japan.
8. S. S. Bhati, T. Macko, R. Brüll, Quantitative comparison of both chemical composition and molar mass distribution of EP copolymers, World Polyolefin Congress, November 2015, Tokyo, Japan.
9. S. S. Bhati, K. N. Prabhu, T. Macko, R. Brüll, Quantification of differences in molecular heterogeneities of polyolefins, Blue Sky conference on catalytic olefin polymerization, June 2016, Sorrento, Italy.

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26. September 2016

**Eidesstattliche Erklärung**

**Affidavit**

Ich erkläre hiermit, dass ich meine Dissertation selbstständig und nur mit den angegebenen Hilfsmitteln angefertigt habe.

*I hereby affirm that I have prepared my dissertation independently, and only with the specified resources.*

Sampat Singh Bhati

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26. September 2016

Erklärung

Declaration

Ich erkläre hiermit, noch keinen Promotionsversuch unternommen zu haben.

*I hereby declare that I have made no previous attempt to get a PhD.*

Sampat Singh Bhati

**Curriculum Vitae**

## *PERSONAL DATA*

**Name:** Sampat Singh Bhati
**DOB:** 24.09.1990
**Email:** sampatiitr@gmail.com

## *WORK EXPERIENCE*

| | |
|---|---|
| **July 2013 - Sep 2016** | Research Associate at Fraunhofer-LBF, Darmstadt |
| **Jan 2012 - Aug 2012** | Teacher & Co-founder at Pathsala Institute, Saharanpur |
| **May 2011 - July 2011** | Internship at ABO Akademi University, Turku |

## *EDUCATION*

| | |
|---|---|
| **July 2013 - Present** | PhD from TU Darmstadt, Germany<br>Department: Chemistry |
| **July 2008 - June 2013** | Integrated Master's Degree (5 years) from<br>IIT Roorkee, India<br>Department: Polymer and Process<br>Engineering |

## *ACHIEVEMENTS*

- **All India Rank 1** in Graduate Aptitude Test in Engineering (GATE), 2012
- **Merit Cum Means scholarship** for 5 years provided by Ministry of Education, India
- **Prime minister's scholarship** for 4 years provided by Sainik Welfare Department, India

## *SKILLS*

| | |
|---|---|
| **Languages** | English, Hindi, German (elementary), Rajasthani |
| **Softwares** | WinGPC Unity, Origin, Endnote, Windows and Microsoft Office |
| **Techniques** | HPLC, GPC, 2D-LC, CRYSTAF, TREF, DSC |

Sampat Singh Bhati 26.09.2016